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MOTORENKRAFTSTOFFE UND DER UMWELTSCHUTZ

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Die Motorisierung trägt im steigenden Maße der Umweltverschmutzung bei. Hauptverantwortlich dafür sind Kohlenmonoxid, reine und anoxidierte Kohlenwasserstoffe, karzerogene Polyaromaten, Stickstoffoxide, Schwefeloxide, Bleiverbindungen und die sekundär hervorgerufenen Stoffe wie Ozon, Peracylnitrate, singletter Sauerstoff und Smog-Feststoffe. Es werden Maßnahmen diskutiert, die von Seite der Kraftstofferzeuger zu unternehmen sind, um die Umweltverschmutzung durch Auspuffgase der Kraftfahrzeuge auf ein erträgliches Niveau herabzusetzen.

Die weitere Entwicklung der Motorenkraftstoffe in unseren Ländern sowie in der ganzen Welt wird durch die Rücksichtnahme auf die Umwelt in großem Maße beeinflusst werden [1]. In den USA beteiligt sich die Motorisierung an der Luftverschmutzung mit etwa 44 %, in Westeuropa mit 25-30 %, in der ČSSR z.Z. mit 12 bis 20 % gleich ob Land oder Stadt. Dieser Anteil wächst ständig. In den USA entfallen 13, in der ČSSR 8 PKW auf 1 km². Auch wenn die Motorisierung bei uns bisher noch nicht den erschreckenden amerikanischen Ausmaß erreicht hat (1 PKW pro 2 Einwohner, in der ČSSR pro 13 Einwohner), sind unsere Sorgen um die Erhaltung einer sauberen Umwelt nicht weniger akut als in den USA.

Der Umweltschutz fordert die Unterdrückung folgender Pollutanten in den Auspuffgasen: Kohlenmonoxid, Schwefel- und Stickstoffoxide, unoxidierte, anoxidierte und gespaltene Kohlenwasserstoffe, kanzerogene Polyaromaten, Ruß und Bleiverbindungen.

Kohlenmonoxid ist ein bekanntes Gift.

Die reinen, anoxidierten und gespaltenen Kohlenwasserstoffe sind lästig durch ihren Geruch. Einige von ihnen sind kanzerogen. Olefine, Aromaten und Stickstoffoxide fördern in sonnenbelichteten Gegenden die Bildung des weißen Smogs und der gesundheitsschädlichen starken Oxidanten (Ozon, Peracylnitrate, singletter Sauerstoff).

Stickstoffoxide sind in erhöhten Konzentrationen, die allerdings z.Z. nicht durch Auspuffgase erreicht werden, toxisch.

Schwefeloxide greifen die Gesundheit, Ernte und Materialien an. Sie begünstigen die Bildung von Nebel.

Ruß im schwarzen Rauch belästigt die Umwelt. Er kann sogar den Verkehr verhindern. An seiner Oberfläche adsorbieren sich Stoffe, die kanzerogene Wirkung haben.

Blei ist ein Gift.Zwar bestreiten einige ernste wissenschaftliche Instituten die Möglichkeit, daß Blei in Auspuffgasen die Gesundheit des Menschen gefährden könnte. Es überwiegen jedoch entgegengesetzte Meinungen, die zusammen mit anderen Faktoren zur Herabsetzung sogar bis zur völligen Abschaffung des Bleies im Benzin drängen.

Kohlenmonoxid und Kohlenwasserstoffe sind Produkte der unvollkommenen Verbrennung der an Kraftstoff reichen Gemischen, die typisch für die derzeitigen Ottomotoren sind. Ruß, anoxidierte und gespaltene Kohlenwasserstoffe sind Produkte der unvollkommenen Zerstäubung des Kraftstoffes in der Brennkammer des Dieselmotors bzw. der unvollkommenen Verbrennung im Zweitakt-Ottomotor. Die Stickstoffoxide entstehen durch direkte Synthese aus dem Sauerstoff und Stickstoff der Verbrennungsluft. Ihre Bildung wird durch hohe Temperaturen gefördert. Die Schwefeloxide stammen aus schwefelhaltigen Verbindungen, die vor allem in Dieselkraftstoffen vorhanden sein können.

Gegen diese Pollutanten werden von Konstrukteuren Maßnahmen in der Konstruktion des Motors gesucht. Auf Einzelheiten wollen wir nicht eingehen. Wir wollen uns nur mit der Feststellung begnügen, daß diese Anstrengungen außerordentlich wichtig sind. Es ist allerdings unsicher, ob es gelingen wird, ohne Einbau von Zusatzeinrichtungen für Auspuffgase auszukommen, die die Pollutanten entfernen d.h. ohne Einbau von Filtern für Bleiverbindungen und von thermischen bzw. katalytischen Reaktoren für die Nachverbrennung von CO und Kohlenwasserstoffen und die Beseitigung von Stickstoffoxiden. An diesen Geräten wird eifrig gearbeitet, aber trotz einiger Erfolge ist die Entwicklung noch nicht abgeschlossen. Mit der allgemeinen Einführung dieser Einrichtungen wird allerdings in den USA ab 1976 und in Europa nach 1980 gerechnet.

Es besteht nun die Frage, wie man die Kraftstoffe den erhöhten Anforderungen von Seiten des Umweltschutzes anpassen muß.

Benzinkraftstoffe

Die Erwägungen über die künftigen Treibstoffe gehen davon aus, inwieweit es durch die erwähnten Maßnahmen gelingen wird, die typischen Pollutanten, vor allem CO, Kohlenwasserstoffe, NO_x und Pb aus den Auspuffgasen zu beseitigen. Es sind drei Grenzfälle zu betrachten:

1. Die erwähnten Einrichtungen werden ausreichen um diese Pollutanten unschädlich zu machen.

2. Diese Einrichtungen werden nur dann ausreichen, wenn bleiarme oder bleifreie Benzine verwendet werden.

3. Auch mit bleifreien Benzinen wird es nicht gelingen die immer strenger werdenden Normen einzuhalten.

Bevor wir die einzelnen Fälle betrachten, wollen wir etwas näher die Eigenschaften der Benzinkohlenwasserstoffe vom Standpunkt der Beziehungen zwischen der Verbrennung und dem Umweltschutz betrachten.

Die n-Alkane haben eine zu niedrige Oktanzahl und verschlechtern die Klopffestigkeit des Benzins. n-Alkane ab C_5 sind weitgehend zu vermeiden.

Die iso-Alkane sind umso wünschenswerter, je verzweigter sie sind. Sie haben hohe Oktanzahl, verbrennen rasch und sauber. Ihre photochemische Aktivität, d.h. die Eigenschaft in der Luft Smog zu produzieren, ist sehr gering. Besonders wertvoll sind von den iso--Alkanen C_5 das Methylbutan, C_6 die Dimethylbutane,C_7 die Dimethylpentane und Trimethylbutan, C_8 die Trimethylpentane und Dimethylhexane, C_9 die Trimethylhexane und C_{10} die Tetramethylpentane, alle Syntheseprodukte.

Von den Cycloalkanen, die ähnlichen umweltschädlichen Verbrennungseigenschaften besitzen, kommen wegen der Oktanzahl nur wenige in Betracht: das Cyclopentan, Methylcyclopentan, Dimethylcyclopentane und als Grenzfall das Cyclohexan. Allgemein werden die höheren Cycloalkane aromatisiert. Wünschenswerter wäre eine Hydrogenolyse zu stark verzweigten iso-Alkanen.

Der beste Kohlenwasserstoff aus der Aromatenreihe ist wahrscheinlich das Toluol. Obwohl das Benzol zwar flüchtiger ist, besitzt es in niedrigeren Konzentrationen eine schlechtere Mischoktanzahl. Höhere Aromaten neigen zur Bildung von Ablagerungen im Motor, zu unsauberer Verbrennung, unkontrollierbarer Zündung und sind photochemisch aktiv. Ihr Aktivitätsindex liegt um 3, wenn iso--Alkane mit 1 bewertet werden. Im allgemeinen sollte ein höherer Gehalt an Aromaten mit einem höheren Gehalt an iso-Alkanen ausgeglichen werden.

Die Olefine sind bei kleinen Geschwindigkeiten klopffest und besitzen bei tieferen Konzentrationen eine sehr gute Mischoktanzahl. Als gute Vertreter gelten die Mono- und Dimethylbutene, die Methyl- und Dimethylpentene und Trimethylpentene. In hohen Konzentrationen verlieren jedoch die Olefine ihre gute Mischoktanzahl und bei hohen Geschwindigkeiten auch ihre Klopffestigkeit. Sie sind photochemisch sehr aktiv (Index 6).

Aus diesen Gründen ist die Konzentration der Aromaten und der Olefine zu begrenzen. Die Höchswerte liegen für die Aromaten in den USA bei 30 %, in Europa bei 50 %, für die Olefine bis etwa 15 %.

Wir wollen nun die einzelnen Fälle näher untersuchen.

Fall 1 (Blei zulässig)

In unseren Ländern ist die Oktanzahl und das Oktanprofil weiter zu verbessern. Als Hauptprozesse kommen in Betracht die Isomerisierung der Alkane C_5 und C_6 (Oktanprofil!) und das Reformieren von Schwerbenzin. Wünschenswert sind das katalytische Krakken und die Alkylierung von Isobutan.

Fall 2 (Blei nicht oder nur begrenzt zulässig)

Die Forderung nach einer hohen Oktanzahl und einem ausgeglichenen Oktanprofil bleibt bestehen. Wünschenswert wären Antiklopfmittel auf einer anderen als Bleibasis, ungefähr gleich wirksam wie Blei,prieswert und zugänglich, untoxisch, ohne schädliche Wirkung auf den Motor und auf die Nachverbrennungsunrichtungen einschließlich Katalysatoren. Die Suche nach einem solchen Antiklopfmittel ist bisher erfolgsarm, geht allerdings noch weiter. Die wünschenswerten Produkte auf Eisenbasis (Eisenpentakarbonyl, Ferrocene [2-5] geben zwar untoxische Verbrennungsprodukte, haben aber andere schwere Nachteile. Sowjetische (Nesmejanow-Schule) und amerikanische Arbeiter (Ethyl Corporation) glauben an Methylcyclopentadienylmangantricarbonyl einen gleichwertigen Ersatz für Bleialkyle gefunden zu haben. In Bezug auf Antiklopfwirkung ist diese Verbindung sehr wirksam [6]. Ungelöst scheinen die Probleme des Austragens der Verbrennungsprodukte, der Wirkung auf die Nachverbrennungskatalysatoren und der Toxizität zu sein. Nichtmetallische Antiklopfmittel aus der Reihe der aromatischen Amine könnten in Frage kommen für Benzine mit bereits einer hohen Grundoktanzahl [6].Ungelöst ist ihr Einfluß auf die Bildung von Stickstoffoxiden. Alkohole sind weniger wirksam,als die Amine. Sie können als Zusatzstoffe gegen Vergaservereisung dienen mit günstiger Wirkung auf die Oktanzahl [6]. Es sei noch die direkte Einspritzung vom Wasser in den Verbrennungsraum zu nennen. Diese in den Flugzeugmotoren bewährte Technik ist sympathisch, da das Wasser die Neigung zum Klopfen unterdrückt, die Verbrennungstemperatur herabsetzt, die kohlenstoffhaltigen Rückstände im Verbrennungsraum vergast und die Katalysatoren in Nachverbrennungseinrichtung nicht schädigt [7]. Ungelöst sind viele Konstruktionsprobleme, sodaß das Wasser bisher die sog. "drivebility" des Fahrzeuges beeinträchtigt.

Sollte es nicht gelingen einen gleichwertigen Ersatz für Bleialkyle zu finden - er ist vielleicht auf dem Gebiet der homogenen Katalyse zu finden -, so ist ein anderer Weg zu wählen und zwar der Weg der bleifreien aromatischen Benzine mit thermischer oder katalytischer Nachverbrennung der Auspuffgase. Als Prozesse kommen in Betracht wiederum die Isomerisierung der n-Alkane C_5 und C_6, ein scharfes Reformieren des Schwerbenzins mit einer weitgehenden Beseitigung der restlichen n-Alkene. Über das katalytische Kracken und die Alkylierung von Isobutan gilt das gleiche wie im Falle 1.

Fall 3 (Blei unzulässig, strengste Normen für den Umweltschutz)

In diesem Falle müßte man den kostspieligsten Weg zum bleifreien oder bleiarmen Benzin wählen. Die photochemische Aktivität der Olefine und Aromaten und die Kanzerogenität der Polyaromaten müßten berücksichtigt werden. Katalytische Nachverbrennungsreaktoren würden unentbehrlich sein. Es müßte höchstwahrscheinlich aliphatische Kohlenwasserstoffe zur Benzinerzeugung gewählt werden; eine vollkommene Umwandlung der n-Alkane C_5 und C_6 wie im Fall 1 und 2, Hydroformieren des Schwerbenzins und Hydrocracken der schweren Erdölfraktionen zu Isobutan, Isopentan und Isohexane, Alkylierung des Isobutans mit Olefinen C_2 bis C_4,vorzugsweise mit Äthylen, aus der Pyrolyse oder Dehydrierung, beschränkte Aromatisierung des Schwerbenzins mit nachfolgender Demethylierung der Alkylaromaten zu Toluol und Benzol. Die leichtesten und schwersten Bestandteile des Benzins müßten beseitigt werden. Ein solches Benzin propagiert die General Motors: OZ (Research) 91 (Minimum),Dampfdruck 630 mbar (Maximum), Olefine 15 % (Maximum), Blei nicht über 0,02 %, 10 % des Benzins sollten zwischen 55 bis 65 °C, 50 % um 90 °C und 90 % bis 120 °C überdestillieren.

In allen drei Fällen wird nach den derzeitigen Vorstellungen mit Nachverbrennungsreaktoren für Auspuffgase gerechnet, wobei im Fall 3 die katalytischen Reaktoren bevorzugt werden.

Dieselkraftstoffe

Aus den Auspuffgasen der Dieselmotoren müssen der Ruß (der schwarze Rauch), die unverbrannten, anoxidierten und gespaltenen Kohlenwasserstoffe (der blaue Rauch), die Stickstoffoxide und die Schwefeloxide weitgehend verschwinden.

Als wichtigste Maßnahmen sind eine gute Zerstäubung des Kraftstoffes,eine sorgfältige Instandhaltung der Zerstäubungsorgane und eine genügende Leistungsreserve des Motors zu nennen. In der ČSSR werden z.B. ab sofort 7 PS und ab 1974 8 PS pro 1 t Last vorgeschrieben.

Von der Seite des Kraftstoffes her wird der Ruß und die unverbrannten Kohlenwasserstoffe durch Herabsetzung des Siedeendes vom gegenwärtigen Wert von 350-360 °C auf max.355 °C herabgesetzt. Den Aromatengehalt wird man wahrscheinlich auf max. 10 % limitieren müssen, z.B. gegebenenfalls durch eine Hydrierung bei tieferer Temperatur. Man wird wahrscheinlich ohne Additive nicht auskommen können. Als solche werden metallorganische Verbindungen, vor allen Manganocene, und Metallsalze, vorwiegend Bariumverbindungen vorgeschlagen oder bereits verwendet. Manganocene sollen die Bildung von Ruß von vorne rein unterdrücken. Die Bariumsalze sollen dagegen das Nachbrennen des bereits gebildeten Russes noch im Motor erleichtern. Dabei sind jedoch schwerwiegende toxikologische Probleme zu lösen. Mangan, das in den Auspuffgasen des Benzinmotors vielleicht harmlos ist, kann bei Dieselmotoren wegen der höheren Konzentration und wesentlich größerer Menge der Auspuffgase bedenklich sein. Das gilt auch für das Barium. Bei Tierversuchen mit Ratten haben sich bis 85 % des verabreichten Bariums in den Knochen abgelagert.

Schwefeloxide in Auspuffgasen können durch eine weitere Herabsetzung des Schwefelgehaltes im Dieseltreibstoff vermindert werden. Bereits heutzutage werden in der ČSSR Dieseltreibstoffe mit 0,2 % Schwefelgehalt verwendet. Eine weitere Herabsetzung ist technisch ohne Schwierigkeiten zu lösen.

Stickstoffoxide können durch Verminderung der Verbrennungstemperatur herabgesatzt werden. Man kann, wie im Benzinmotor, einen Teil der Auspuffgase zurückführen. Man kann auch z.B. Wasser mit dem Kraftstoff im Form einer Emulsion in den Motor einführen [8]. Obwohl das Wasser den Gang des Dieselmotors härter macht, den Zündverzug vergrößert und die spezifische Leistung herabsetzt, verläuft die Verbrennung vollkommener, der Kraftstoff wird feiner verteilt, der Motor bleibt sauberer, die Rauchbildung wird herabgesetzt, der Kohlenmonoxidgehalt im Auspuffgas vermindert, sodaß der spezifische Verbrauch des Kraftstoffes etwas zurückgeht. Ähnlich wie im Benzinmotor sind auch hier mit dem Wasser konstruktive Probleme verbunden.

Ausblick

Alle beschrieben Maßnahmen sind mehr oder weniger kurzfristig. Vom Standpunkt der Motorkonstruktion werden auch andere Lösungen gesucht. In der nahen Zukunft wird mit dem Wankelmotor gerechnet, der bleifreies Benzin verbrennt. Es wird mit Verbrennungsturbinen, Dampfmaschinen, Stirlingmotoren, Elektromobilen experimentiert. Als neuer Kraftstoff wird bereits jetzt Propan und Butan im Stadtverkehr für Taxi und LKW wieder eingeführt. Am Horizont ist Methan in komprimierter oder verflüssigter Form. Es wird sogar an Wasserstoff als idealen Kraftstoff der Zukunft gedacht.Mit dem Bau riesieger Betriebe für Methanolsynthese ist auch Methanol als Kraftstoff zu erwägen. Als ideale Lösung wäre ein mit Brennstoffelementen ausgerüstetes Fahrzeug zu betrachten: es arbeitet mit einem hohen Wirkungsgrad, der im Gegensatz zum Otto-Motor mit fallender Leistung steigt, keinen Lärm erzeugt und keine Pollutanten produziert.

Es ist noch schwer abzusehen, wann diese Vorschläge die technische und ökonomische Reife erreichen werden.

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SUMMARY

The reduction of pollutants from the exhaust gases from combustion engines can be achieved by improvements in the engines, by use of filters, thermal or catalytic reactors for exhaust gases and through improved fuels.

For gasoline three cases are discussed:

a) the presence of the lead in the gasoline is not harmful to the environment: actual processes can still be used, e.g. the isomerization of n-alcanes and the reforming of naphthas

b) the content of lead must be sharply reduced or eliminated: new antiknock additives are desirable, but all of them on the basis of Fe, Mn, aromatic amines, alcohols or water have some drawbacks; the way to aromatic gasolines seems to be indicated

c) the content of lead must be nil, regulations are getting still stronger: the way to aliphatic gasolines seems to be the best.

For diesel fuels the distillation end, the content of aromatic and sulfur compounds must be sharply reduced, additives against the formation of soot be used - but here still problems are open. The combustion temperature should be lowered, for instance through the use of water.

Perspectives are shortly rewieved. Combustion cells seem to present an ideal solution to the environment problems, but their use is still remote.

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L'ÉLIMINATION DU SOUFRE PROVENANT DE LA COMBUSTION DES PRODUITS LOURDS, PAR DÉSULFURATION DES COMBUSTIBLES ET DES FUMÉES

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Après une revue de la tendance générale en France de la teneur en S des fuels on donne une comparaison de l'évolution de la réglementation et des spécifications dans différents pays. On compare ensuite les méthodes de désulfuration directe et indirecte des résidus (hydrocarbures lourds) en insistant plus particulièrement sur les consommations d'hydrogène et sur une nouvelle méthode de calcination désulfurante du coke de pétrole permettant d'utiliser économiquement le "delayed coking" comme procédé de désulfurisation des résidus. Sont donnés ensuite comparativement des chiffres de l'économie de la désulfurisation des fumées et en conclusion, la variation du prix du fuel (aux USA, N.Y.C.) en fonction de sa teneur en S.

Il m'échoit le redoutable mais néanmoins agréable honneur de prononcer une Conférence au Jubilé de MÁFKI, sur un sujet de mon choix. Beaucoup de liens m'attachent à MÁFKI, dès sa fondation, et je crois y compter de nombreux amis. Aussi je me suis permis de choisir un sujet d'actualité, relativement contreversé à la fois sur le plan scientifique, technique et économique, mais dont j'ai eu l'occasion de faire part de mes réflexions à mes Collègues français, lors du dernier Congrès National à Biarritz le 24 Mai 1973. J'ai pensé que le sujet était ou sera tôt ou tard aussi d'actualité pour la Hongrie.

TENDANCES GENERALES EN FRANCE

La capacité de raffinage avec 24 Raffinieries en 1972 a atteint en France 144.910.000 t/an pour 119.959.000 t/an de produits raffinés en 1972. L'évolution de la production entre 1973 et 1980 des fuels (domestiques et lourds), est estimée comme indiquée sur la Figure 1. Elle passe de 30 millions de t/a en 1973 à 55 millions de t/a en 1980 pour FOL et respectivement de 35 millions de t/a à 66 millions de t/a pour le FOD.

Il faut noter que la capacité de dèsulfuration des distillats semble être restée constante entre 1970 et 1971 a seulement environ 13 millions de t/a. Ceci est sans doute dû au ralentissement assez net de l'accroissement de la capacité du raffinage dans son ensamble qui, tout en dépassant pour la première fois 100 millions de t/a en 1971 n'a progressé entre 1970 et 1971 que de 6 % alors qu'elle progressait de 13 % l'année précédente.

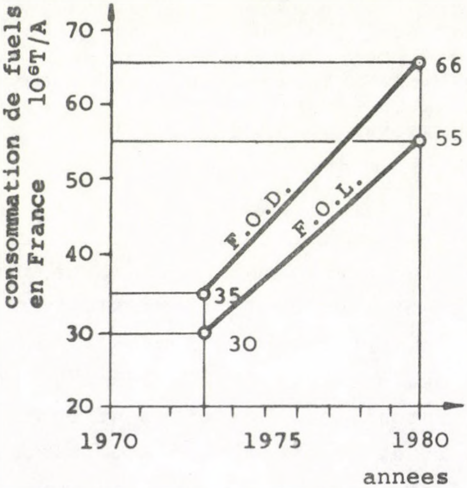

Fig. 1. Reference l'union des chambres syndicales de l'I.P. (Rapport 1971)
F.O.D. (Fuel oil Domestique)
F.O.L. (Fuel oil Lourd)

On avait expliqué en partie ce ralentissement précisément par une expansion moins rapide que prévue de la demande du fuel oil domestique. Vu les prévisions actuelles dans la perspective 1980 (Figure 1), il est peu probable que cette tendance soit maintenue et on peut prévoir, au contraire, une augmentation certaine d'une part de la capacité de désulfuration des distillats (y compris distillats lourds), et, d'autre part, un accroissement du pourcentage des produits lourds dans la production des raffineries. (Ces produits FOD - FOL, bitumes, lubrifiants et divers, représentaient en 1960 plus de 40 % mais descendaient progressivement jusqu'en 1968 à 35 % pour recommencer à croître et atteindre en 1971 à nouveau plus de 38 %. Il est à prévoir qu'en 1980, ils atteindront à nouveau plus de 40 %.)

La teneur en soufre des coupes lourdes de 2,3 % en moyenne en 1972 en France, dépend du pétrole brut dont elles sont originaires et des traitements physico-chimiques qu'elles ont subis.

L'évolution de l'origine des pétroles bruts traités dans nos Raffineries est indiqué sur la Figure 3 bis.

Je ne voudrais indiquer ici qu'avec la diminution du pétrole brut algérien que nous traitons (26 Millions T/A) en 1970 et seulement 9,1 Millions T/A en 1971 et 11,2 Millions en 1972 , et malgrè l'accroissement des bruts nigeriens (5,2 Millions T/A en 1970, 12,3 Millions T/A en 1971 et 14 Millions T/A en 1972) et Lybien (15,3 Millions T/A en 1971 et 10 Millions T/A en 1972), la part de plus en plus grande prise par les bruts riches en soufre du Moyen - Orient (44,5 Millions T/A en 1970, 63,4 Millions T/A en 1971 et 77,6 Millions T/A en 1972) - nous oblige à considerer le problème de désulfuration avec une attention accrue.Il est certain que si nous manquions en France d'approvisionnement et de pétrole brut à faible teneur en S, la teneur moyenne en S des combustibles lourds passerait et d'ici 1980 à 3 % environ.

EVOLUTION de la REGLEMENTATION et des SPECIFICATIONS

Je voudrais signaler une étude remarquable consacrée à ce sujet déjà en 1970 par un des anciens Présidents de l'A.F.T.P.* M.P.A. LAURENT (C.F.R.) avec M.W.C. HOPPER [26], dans le cadre du "STICHTING CONCAVE" de la Haye pour une Conférence tenue à GENEVE en Novembre 1970 par une Commission Economique pour l'Europe des Nations Unies pour les problemes de la Pollution atmosphérique. (Rap. 25/70). On estimait déjà à l'époque que l'émission mondiale de SO_2 représentait 146 Millions de T/A en 1965 (dont 93 % dans l'Hémisphère Nord), et passerait à 196 Millions de T/A en 1980, et 333 Millions T/A en l'an 2000, si on n'introduisait pas de mesures de contrôle et de règlementations nouvelles.

20 % de cette émission étaient dûs aux produits pétroliers responsables pour 40 % de la production mondiale de l'énergie; ce dernier pourcentage passera à 50 % puis à 60 % en 1980.

On a pu estimer que la quantité de SO_2 rejeté dans l'atmosphère en France passera de 1.400.000 T/an en 1972 à 2.700.000 T/A ou 3.400.000 T/A en 1980, en l'absence de toute élimination de S.

Pour maintenir la quantité de SO_2 rejeté en 1980 au niveau de 1972 (et pour respecter les concentrations admises au sol), il faudrait éliminer entre 650.000 et 1.000.000 de T/A de S des combustibles lourds produits en France.

Sans entrer dans le détail, on peut préciser qu'en Europe Occidentale, il y a 5 Catégories de pétroles bruts classés suivant la teneur en S des résidus (360^o +) allant de <1 % à > 4,5 %. (Cat. V. Venezuela). Il a été montré qu'en Europe Occidentale, ce sont pour 80 % les combustions de fuels oils qui sont responsables pour les émissions de produits sulfureux dans l'atmosphère.

Les législations en vigueur limitant la teneur en S des fuels oils et/ou de l'émission du SO_2 (et sa concentration au niveau du

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*A.F.T.P. = Association Francaise des Techniciens du Pétrole sol), varient en Europe de pays en pays. Par exemple, la législation en SUEDE prévoit une limite générale de 2,5 % S avec une limite de 1 % max. de S par exemple pour Stockholm.

En Allemagne de l'Ouest, de Land de Westphalie/Rhin Nord impose aux installations de plus de 800.000 Kcal/H et dans certaines zones industrielles, un fuel ayant au maximum 1,8 % de S.

En Italie, la législation prévoit la limitation des fuels lourds à haute teneur en S dans les installations de faible importance.

En Norvège, à Oslo par exemple, des installations consummant jusqu'à 700 T/A de fuel doivent utiliser du fuel à moins de 0,8 %; les plus grandes installations peuvent aller jusqu'à 2,5 % de S.

Aux U.S.A., le "Clean Air Act" [22] et les règlementations assez draconiennes du Japon [23] ont été assez abondamment decrites dans la littérature pour qu'on ne les detaille pas ici.

Un Tableau (Figure 2) indique à titre de comparison quelques règlementations en vigueur recommandées ou suggérées dans différents pays pour les émissions de SO_2 (Seule apparemment en Allemagne, existait en 1970 déjà une règlementation en vigueur).

On voit que la règlementation, sans être encore uniforme est de plus sévère, et tend à l'être encore plus en Europe et au Japon dans les régions à forte population qu'aux U.S.A. (Ex. Allemagne, Suede, Hollande, Pays de l'Europe, de l'Est, etc. ...).

Malgrè une tendence que l'on prévoit en baisse, (à l'échelle de l'OECDE) entre 1970 et 1975 pour la teneur moyenne en soufre des résidus (360^{o} +) - (Voir Figure 3), il y a une augmentation (de 2,10 à 2,30 %) prévue entre 1975 et 1980 [26], avec un "minimum" vers 1975 (basée sur une répartition des importations de pétrole brut comme indiqué sur la Fig. 3 Bis).

Les restrictions et règlementations ne font, évidement, qu'augmenter dans tous les pays européens, y compris la France (Voir Tableau N^{o} 1) pour les spécifications des gas oils et fuels, les limitations ne jouent pas seulement directement par la teneur

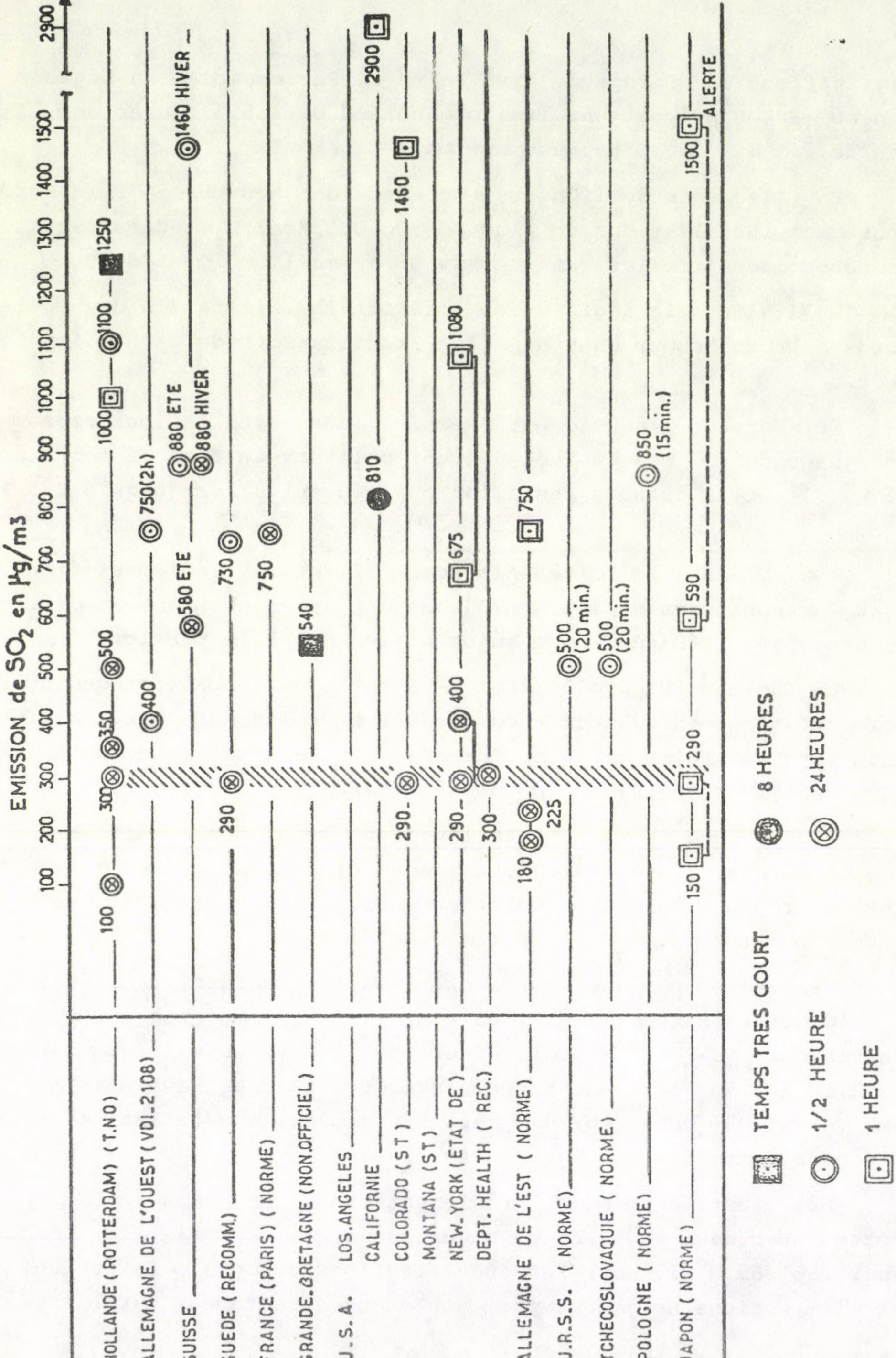

Fig.2. Reglementation des emissions de SO_2 en differents pays

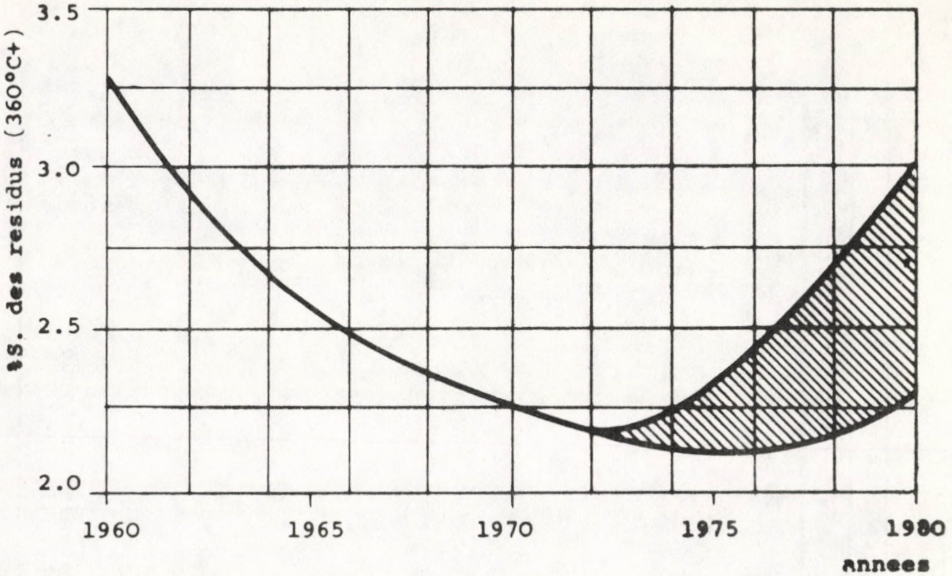

Fig. 3. Evolution de la teneur moyenne en S. des residus (360°C +) dans les pays de l'O.E.C.D.E *Basee surla Fig.3 bis: repartition des approvisionnements en brut).
A - Au cas de manque d'approvisionnement en brut a faible teneur en S.

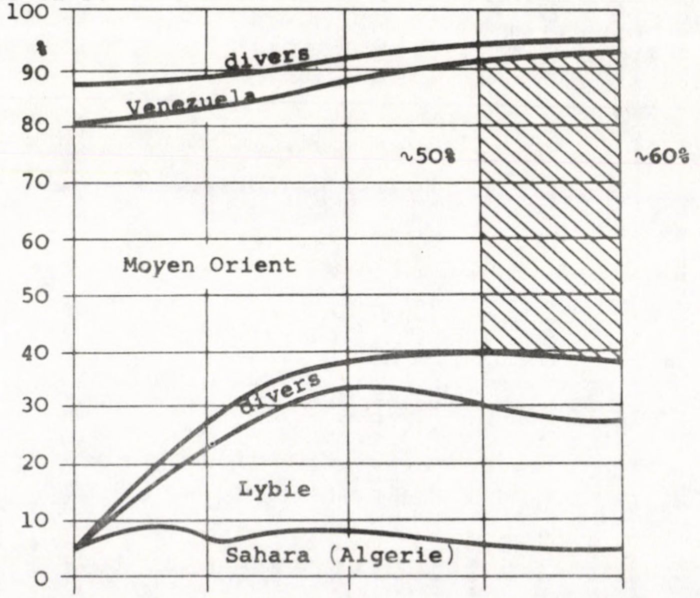

Fig. 3 Bis. Evaluation faite en 1967 de l'evolution des approvisionnements en petrole brut des pays de l'O.E.C.D.E.

Tableau N° 1. Specification de la teneur en S(PDS) admissible pour les fuels et gas oils en differents pays europeens

Pays ()	Normes	Gasoil	Fuels oils: max. S PDS.				
			Extra leger	Leger	Moyen	Lourd	Extra lourd
Autriche	ÖNORM C 1108	1.0 (0.5)	-	1.5 (0.9)	2.5 (1.3)	3.5 (1.3-1.6)	-
Belgique	NBW 52501	1.0	-	1.5	2.7	3.0	4.5
Finlande	-	-	-	-	-	-	-
Danemark	-	-	-	-	-	-	-
France	Decret ministeriel 30.4.68-18.9.67-30.12.66	0.5	-	2.0	2.0	4.0	-
	LOI 61.842 du 2.8.[illegible]	(0.4)	-	-	-	-	-
Paris	arrete 11.8.64 supp. LOI: 61-842	-	-	-	-	-	-
Allemagne	Din 51603 GW.B.O/ind.code	-	0.8	-	-	2.8	-
	§ 16,24 et 25		(0.25-0.55)			(1.8-2.0)	
Grece	-	-	-	-	-	-	-
Italie	Decret min./LOI:615 13.7.1966	1.0	2.5	3.0	4.0	4.0	-
Hollande	-	-	-	-	-	-	-
Norvege	-		0.5 < 700 T/A - 2.5 (> 700 T/A)				
Portugal	-	-	-	-	-	-	-
Espagne	Decret 2107/1968 du 17.8.1968						
Madrid			2.6 % usage domestique 2.0 % (apres 1970)				3.0 % usage indust.

() = qualite des livraisons habituelles

en S mais aussi par la viscosité. Par exemple, à PARIS, les Arrondissements ler, 2ème, 8ème, 9ème et 17ème et partie des 10ème, 16ème et 18ème, constituent la zone N° 1, le restant la zone N° 2. En zone 1, la concentration du SO_2 dans les gaz de combustion ne doit pas dépasser 2 g de S (Thermie du fuel consommé, ce qui, pratiquement, limiterait la teneur en S à 2 % pds, admettant un pouvoir calorifique de 10.150 cal/g. mais la restriction placée sur la viscosité en zone 1 et pour les foyers de moins de 350 Thermies/H. en zone 2, limite pratiquement la teneur en S à < 0,5 % pds (du fuel léger ayant une viscosité de 2,5° E à 50° C (17 c-S à 50° C) n'est utilisable en zone 2 que pour des foyers à plus de 350 Thermies/H et le fuel oil N° 1 à 14° E a 50° C pour plus de 500 Th/H.) [27, 28 35].

Il s'avère donc certain que les limitations imposées par l'évolution de la règlementation (émission SO_2 teneur S) imposeront à la fois aux raffineurs la production de fuel oil à des teneurs en S ramenées: à 1 % et en-dessous et aux utilisateurs des méthodes d'épuration des fumées pour diminuer l'émission de SO_2.

Evidemment, le problème pout se poser autrement à de très "grands" utilisateurs comme, par exemple, l'E.D.F.* qui peut avoir un intérêt économique à brûler du fuel à relativement haute teneur on S puis épurer les fumées (en récupérant le S), ou, par exemple, gazéifier du fuel, désulfuriser les gaz et disposer s'il y a lieu, du résidu contenant une partie importante du soufre [29, 34, 34 bis].

On semble donc bien s'orienter sur deux grandes qualités de fuel:

$$**BTS \leq 1\ \%\ S \quad \text{et} \quad **HTS \leq 3,5\ \%\ S$$

(avec probabilité que dans les zones de forte densité de population et industrielle, la teneur en S devrait descendre tôt ou tard vers 0,5 %). E.D.F. semble envisager trois qualités:

$$< 1\ \%\ S \quad < 2\ \%\ S \quad \text{et} \quad < 4\ \%\ \text{de}\ S$$

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*Electricité de France

**BTS = Basse Teneur en Soufre
HTS = Haute Teneur en Soufre

et brûlera quelques 25 Millions de T/A de S vers 1980 [14]-[34 Bis] -[25].

En l'absence d'une règlementation (et de spécifications) homogènes en Europe Occidentale, il est donc probable qu'on évoluera non pas exactement comme au Japon où on a fixé une teneur maximale en S des combustibles, mais plutôt comme aux U.S.A. On fixera les règlementations en fonction de la densité de population des zones et des capacités des foyers brûlant du fuel. Par exemple, dans certaines zones à faible densité de population ou dans les foyers (centrales) à grande capacité (ou par exemple des installations d'épuration de fumées peuvent être prévues d'une manière économique), on pourra brûler du fuel ordinaire. Une règlementation généralisée pour la C.E.E. serait très souhaitable.

Une relation reste algébriquement inaltérable et certaine: celle de la teneur en SO_2 des fumées suivant la teneur en soufre du fuel comme indiqué au tableau suivant.

Teneur en S pds %	ppm SO_2 dans les fumées
0.5	300
1.0	600
2.0	1200
3.0	1800
4.0	2400
5.0	3000

On est dons obligatoirement conduit à éliminer le S des fuels et/ou éliminer le SO_2 des fumées.

DESULFURATION DIRECTE et INDIRECTE des RESIDUS

a) Nous avons étudié six [6] 6 variantes de schémas de raffinage incorporant différentes méthodes de désulfuration basant notre raisonnement sur un résidu atmosphérique de KUWAIT à 4 % de S, combinant la distillation sous vide (DCV) Reforming Catalytique (R.C.) l'hydrodesulfuration (HDS), le désasphaltage au propane (DAP), le "Delayed Coking" ou le "flexi coking" (ESSO) et on a montré comment et a quel prix on arrive à abaisser la teneur en soufre des résidus de 4 % à 2,6 %; 1,1 %, 1 %, 0,5 %, 0,56 % ou même 0,25 %. Les coûts s'échelonnent de 1000 à 1500 FF/T de S enlevé.

b) Au sujet des procédés de désulfuration directe (hydrodesulfuration des résidus), un grand nombre d'informations existent pour différents procédés d'hydrodesulfuration des résidus (y compris l'Hydrochracking), de SHELL - CHEVRON [7], ESSO, B.P., KELLOGG-HOC [20] - [13] - [15], U.O.P. = ISOMA [1] - [2] - [3] - [4] - [5] - [6] - GULF [40], [32], HYDROCARBON RESEARCH - CITIES SERVICE, etc.) au sujet desquels un très grand nombre publications existent dans la littérature technique et qu'on ne dètaillera pas ici autrement.

Il semble toutefois que, seulement 7 ou 8 installations ont été réalisées à l'échelle industrielle dont, par exemple, la récente installation de la SHELL - KOPPARTRANS en Suède de 400 T/J opérant à 100-200 atm. et 400° C, récupérant 5 à 10 T/J de S, et éliminant 40 % de la teneur en S du résidu traité.

D'autres installations connues sont, par exemple, KASHIMA - - OIL (Japon) - (45.000 B/J), SHUAIBA (Kuwait) (35.000 B/J).

Je voudrais faire remarquer seulement au sujet de la désulfuration par hydrotraitment des résidus en plus de l'amélioration du "Design" (conception) et des catalyseurs assez amplement décrits par les vendeurs de procédés, le rôle économiquement très important que joue la consommation d'hydrogêne (50 % du prix du traitement par Hydrochracking), et le bilan hydrogène de la raffinerie.

Une "Table Ronde" que j'ai eu l'honneur de présider, a été consacrée par l'A.F.T.P. (publiée dans ia Revuc de l'A.F.T.P. N° 205 - Janvier-Février 1971), à la production d'hydrogène le 9/VI/1970.On y précisait que l'hydrogène peut coûter jusqu'à 0,10

F/m³ (prix 1970) mais son prix pe être abaissé de 50 % si on le produit dans de grandes installations autonomes (par exemple de plus de 1 Million de m³/J).Or, la raffinerie de l'avenir en France sera une raffinerie de l'ordre de 10 Millions de T/A (il y en aura probablement 20 vers 1980). Les raffineries de l'avenir exigéront environ 350 à 500.000 m³/J d'hydrogène par million de T/A de capacité l'Hydrocracking demande jusqu'à 700 m³/T/J traitée, soit 3,5 à 5 Millions m³/J! Même avec l'hydrogène récupéré des Reforming Catalytique, les unités autonomes d'hydrogène seront de capacité telle que la production se fera dans des conditions économiques.

Par contre, les investissements dans ces types de raffineries dépasseront probablement 1300 $/B/J de brut traité (ils étaient entre 600 et 750 $/B/J en 1968).Il n'est donc pas étonnant que le Comité de l'Energie du Parlament Européen ait estimé que vers 1980 l'Europe Occidentale aura investi 2.500 Millions de $ pour permettre de réduire à 1 % la teneur en S des fuels. (La part de la France serait estimée par l'Auteur de l'ordre de 350 Millions $).

(Ce chiffre peut être obtenu aussi à partir du coût estimé en France pour une installation de désulfuration des résidus de 2.500.000 T/A éliminant 75.000 T/A des S représentant 200 Millions de F.F. [10] - [21]), pouvant aller jusqu'à 3 Milliard de F.F.

c) La désulfuration indirecte (Cracking et Gazeification) est aussi traitée abondamment dans la litérature. Je ne veux donc pas aborder ce sujet en détail ici. Je voudrais toutefois faire une remarque étant donné qu'il s'agit d'un procédé très récent développé et industrialisé depuis un an seulement par ma Société mais qui peut avoir une relativement grande importance sur l'aspect économique du "Delayed Coking" en tant que désulfuration des résidus.Généralement, la cokefaction retardée ("Delayed coking") n'est pas poussée aussi loin que p.ex. le "flexicoking (ESSO) [30] en lit fluidisé.

Le "Green coke" obtenu contient généralement 50 % de la teneur en soufre de la charge. Si on opère avec des charges riches en S on obtient du "green coke" de 4 à 6 % de S qu'on juge normalement inutilisable pour produire par calcination du "needle coke";

celui-ci n'est utilisable pour la fabrication des électrodes (aluminium, ferroalliages, etc.) que si sa teneur en S est inférieure à 1 % de S pds. Le "green coke" à 4-5 % de S se vend donc comme combustible à 15-20 $/T et on utilise pour la calcination normalement un coke à faible teneur en S (par exemple 1,5 % de S). Le coke calciné à < 1 % de S se vend à 50-60 $/T (et le coke vert à 1,5 % de S à 25-30 $/T.Or nous avons mis au point, à l'échelle pilote, et breveté un procédé de Calcination desulfurante de coke, permettant d'utiliser un "green coke" à 4-5 % de S et produire un "needle coke" à moins de 1 % de S. avec toutes les autres qualités requises pour un coke à électrodes (densité plus de 2,05; conductibilité électrique 500 Ohm/mm²/m etc.). Une installation industrielle de 100.000 T/A est en construction on Egypte. Le contrat a été signé il y a un an, après essais satisfaisants sur des échantillons de coke provenant des pétroles du Moyen Orient.

Nous pensions que ce fait méritait d'être signalé quand on sait que l'Europe, en général, est importateur de coke pour électrodes et,qu'en France en particulier, ELF avec CONTINENTAL CARBON prévoit le construction d'une grosse installation de calcination du coke. Ce procédé peut, en outre, faire revoir le "delayed coking" pour la désulfurisation avec une optique nouvelle. Depuis qu'il a été signalé en Mai 1973, on a recu à son sujet un três grand nombre de demandes des USA, d'Europe (Allemagne, France, Autriche etc.) d'Extrême Orient (Japon, Indes etc.).

LA DESULFURATION des FUMEES

Là encore, la documentation technique abonde en détails sur des procédés de plus en plus nombreux.

Je voudrais seulement faire remarquer que quelques 87 Procédés et brevets furent dénombrés récemment [9], [38], [12], dont:

- 26 par absorption des fumées par des produits solides inorganiques, solutions et suspensions,

- 34 par absorption dans des solutions organiques,
- 17 par procédés d'oxydation, adsorption variés (régénérables et non,
- 10 par procédés variés avec récupération sous forme de S, SO_2 concentré, H_2SO_4, etc.).

Il faut se concentrer, dans ce domaine, sur les procédés effectivement industrialisés, dont il existe une vingtaine et on peut souligner l'intérêt de celui développé par, l'I.F.P.* En France, la S.N.P.A.s'est attachée à un aspect particulier de la désulfuration des fumées qui est loin d'être négligeable puisqu'il concerne l'épuration des gaz de queue des unités CLAUS qui sont une partie importante des schémas de désulfuration pour la récupération du [9]. -(Voir aussi KELLOGG [12], SHELL [24], [31], [37], etc.)

DONNEES ECONOMIQUES

Il est évidemment extrèmement malaisé de faire des comparations économiques des procédés cités, vu le très grand nombre de facteurs dont tous ne sont pas techniques et économiques. On a pu dire, toutefois, que - toutes choses égales - les méthodes de désulfuration directe et indirecte conduisent à des frais de traitement variant entre 900 et 1.800 F/T de S enlevé tandis que pour l'épuration des fumées, le traitement coûte environ 940 F/T de S enlevé (sans valorisation du S),et 835 F/T (avec valorisation du S à 100 F/T). (Par exemple, SHELL a donné récemment [24, 31] pour son procédé SFGD, des chiffres semblables: 900 Frs/T à 1.115 Frs/T). - (Voir aussi [38]).

Dans le premier cas, on s'est basé sur un résidu de distillation atmosphérique du KUWAIT à 4 % de S et la fourchette des prix correspondait à des désulfurations allant de 2,5 % de S à

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*I.F.P. = Institut Francais du Pétrole

0,25 % S (avec et sans valorisation des sous-produits comme: coke, gaz à bas P.C.* etc.). Je crois que les chiffres raisonnables de 4 % à 1 % de S se situent aux alentours de 1.100 à 1.500 F/T de S enlevé avec amélioration possible, par exemple, avec l'abaissement du prix de l'hydrogène. Pour la désulfuration des fumées on s'est basé sur une centrale de 250 MW brûlant 385.000 T/A de fuel à 3,5 % pds S (la teneur en SO_2 de 2.000 ppm pouvant être réduite à 100 ppm environ).

Il est donc à peu près certain que le procédé d'épuration des fumées est actuellement plus économique que le procédé de désulfuration directe ou indirecte. Il a cependant souvent le désavantage de produire des déchets solides difficiles à disposer, ou produire du S ou H_2SO_4 dont la valorisation économique est fluctuante. Par ailleurs, il semble que ces procédés ne soient économiquement applicables qu'à de très gros consommateurs?

Donc, on peut prédire avec certitude que les deux types de procédés coexisteront nécessairement avec tendance, au fur et à mesure de leur multiplication et de leurs applications industrielles, à un abaissement des prix des traitements qu'on ne peut actuellement encore évaluer avec certitude.

CONCLUSIONS

On n'insistera pas ici sur les conséquences de l'augmentation du prix des pétroles bruts, ni sur l'influence de cette augmentation, prévisible et constante, sur le prix des fuels.

Par contre, en guise de conclusions, j'ai pensé utile de motrer, sur la Figure 4, la variation du prix du fuel fonction de sa teneur en S tel qu'on le pratique aux N.S.A. (New York, XII(72) [42].Car la conclusion de ce bref exposé sera que la désulfuration du fuel (qu'on soit obligé de la faire ou qu'elle résulte d'un

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*P.C. = Pouvoir calorifique

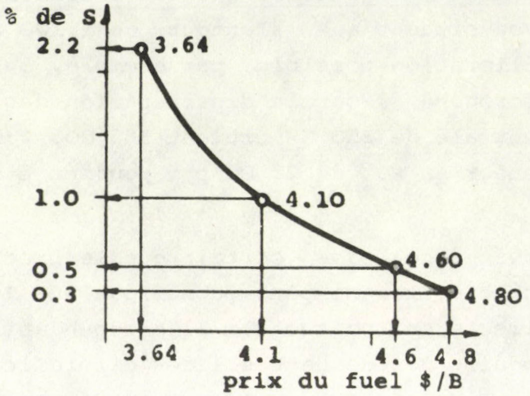

Fig. 4. Prix du fuel aux U.S.A. en Fonction de sa teneur en S (New York; fuel N 6. prix de revendeur par baril 21 XII 1972)

pétrole brut à faible teneur en S, ou que l'on épure les fumées de combustion), doit se payer.

Aux U.S.A., on paie, par exemple, 0,5 $/B* de plus pour un fuel dont la teneur on S est 0,5 % au lieu de 1 % et 0,7 $/B en plus si sa teneur est de 0,3 % au lieau de 0,5 %, mais seulement 0,46 $/B en plus si sa teneur est de 1 % au lieu de 2,2 %. Il faut donc que quelqu'un paie.

Les règlementations imposent, et imposeront encore beaucoup plus dans l'avenir, des investissements importants et des dépenses de fonctionnement non moins importantes aux Raffineurs. Il serait, à notre avis, illogique et économiquement difficilement justifiable dans les Pays Europe Occidentale que seul le consommateur de produits pétroliers déjà lourdement taxé, et les raffineurs dont les marges n'ont fait que diminuer au cours des dernières années, supportent ces lourdes charges.

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*$/B = U.S. Dollars/Barrel U.S.

L'Etat pourrait y contribuer aussi en abaissant les taxes sur les fuels désulfurés et en dégrèvant les investissements (non rentables suivant les critères économiques normaux) des raffineries faites à ce titre, ou encore en facilitant le financement des quelques 3-4 Milliard de Frs dont l'industrie du raffinage du Pétrole aura besoin en France pour des installations de désulfurisation réalisées d'ici 1980/1985.

Dans les Pays de l'Est où le coût de la protection de l'environnement incomble de toute manière à l'état, il nous a semblé qu'il est néanmoins important de connaitre une comparaison économique des méthodes industrialisées d'élimination de Soufre de Résidus lourds, même si elle est faite avec l'optique économique de l'Europe Occidentale.

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SUMMARY

After a review of the general tendancy in France of the S content of fuel oils, the evolution of the regulation and specifications in different countries is described. Direct and indirect heavy oil desulfurization methods are compared, in insisting more specifically on the importance of H_2 consumption and on a new coke

calcination desulfurization process, which allows the economical use of delayed coking as residue desulfurization. Comparativ figures of residue and flue gas desulfurization economics are given. As conclusion, the price variation of heavy fuel oil according to its S content in the USA (N.Y. City) is described.

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TRIBOLOGIE

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Die gemeinsamen Arbeitsgebiete, in denen die Maschinenbauer, Physiker und Chemiker seit Jahrzehnten arbeiten, beginnen sich zu einer einheitlichen Wissenschaft - Tribologie - zusammenzufinden. Umso wichtiger ist es, daß die Spezialisten aller Länder sich über Definitionen, Terminologie und Stoffplan - das Fundament jeder Wissenschaft - abstimmen.

Diese Ausführungen geben Vorschläge zu einem umfassenden Stoffplan von Tribologie und einen zusammenfassenden Überblick über dieses Wissenschaftsgebiet.

EINLEITUNG

Tribologie ist keine neue Lehre. Es handelt sich nicht um das Wachsen eines jungen Fachbereiches, sondern um das Zusammenfinden vieler wichtigen Teilgebiete. Diese existieren unterschiedlich lange und haben sehr unterschiedliche Bedeutung.

Es soll also erreicht werden, daß aus zahlreichen bestehenden Spezialgebieten in der Konstruktion - vorwiegend im Maschinenwesen -, in der Physik und in der Chemie ein einheitliches Fachgebiet entsteht mit gleicher Terminologie, einheitlichen Definitionen, systematischer Gliederung, umfassendem Stoffplan und ausreichender Berufsbildbeschreibung.

1. Tribologie - eine Definition

Unter "Tribologie" soll verstanden werden: Tribologie, die Lehre der Reibung, ihrer Folgeerscheinungen und Folgerungen als Grundlage der Schmierung.

Man könnte ausdrückliche Erwähnung der "Folgeerscheinungen" und "Folgerungen" weglassen, weil man annehmen darf, daß selbstverständlich auch alle Folgeerscheinungen und Folgerungen der Reibung behandelt werden.

Die wichtigste Folgeerscheinung der Tribologie ist der Verschleiß. Seine Bedeutung auf allen Gebieten hat im Vergleich zur Reibung zu einer wesentlich tieferen und breiteren Erfassung seiner Gesetzmäßigkeiten geführt.

Trotzdem ist jede Form des Verschleißes eine Folgeerscheinung eines Reibungsvorganges. Es wäre sachlich nicht richtig, wenn die Verschleißforschung in der Zukunft selbständig bliebe. Daher ist es zweckmäßig das Wort "Folgeerscheinung" in der Definition zu nennen. Auch die Schmierung sollte bei der Definition genannt werden, da heute mit dem Wort "Tribologie" noch nicht automatisch an die Schmierung gedacht wird. Aber es muß auf den richtigen Zusammenhang der Schmierung mit der Tribologie hingewiesen werden, nämlich: Tribologie ist die Grundlage der Schmierung.

Tribologie umfaßt also die Zusammenhänge und Probleme aller Reibungsvorgänge und damit auch aller Folgeerscheinungen und aller für die Technik notwendigen Folgerungen.

Zur Tribologie gehören auch die Folgerungen, die wir auf den tribologischen Grundvorgängen aufbauend zum Nutzen der Maschinen anwenden. Wir zählen zur Tribologie also mit dem Oberbegriff Schmierung auch Schmiertechnik und Schmierpraxis.

2. Tribologie: eine interdisziplinäre Wissenschaft

Tribologie beinhaltet demgemäß Reibung und Reibungsminderung, Verschleiß und Verschleißschutz, Gleitflächenschäden einschlißlich Verschweißen und deren Verhinderung, Schmierung, Schmierstoffe, Schmiertechnik und Schmierpraxis.

Tribologie erfordert meist fachübergreifende Betrachtung, ihre Erkenntnisse liegen in zwischenfachlichen Bereichen der Physik, Chemie und Konstruktion (Abb. 1.).

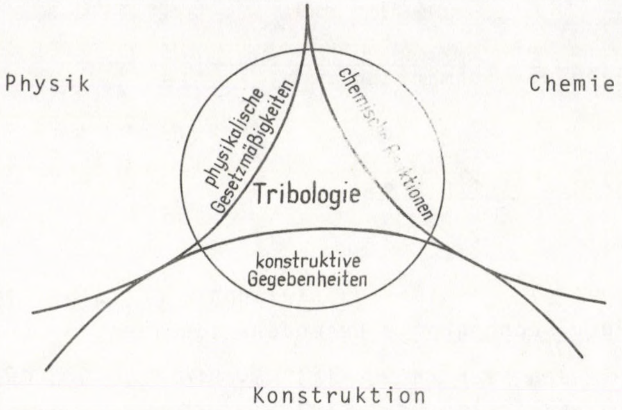

Abb. 1. Tribologie, eine fachübergreifende Wissenschaft

3. Spezialwissen für die Tribologie

Die zu behandelnden Vorgänge sind komplex und schwer überschaubar. Wir haben gesehen, daß Kenntnisse aus drei Fächern erforderlich sind. Neben gewissen Grundgesetzen dieser erwähnten drei Fächer kommen Erfahrungen hinzu aus Metallurgie und Kristallographie, Festigkeitslehre, Strömungslehre und Rheologie, Werkstoff- und Schmierstoffkunde.

Der fundamentale Satz der Schmierung lautet: Alle Vorgänge der Schmierung werden nur dann zufriedenstellend die Reibung und den Verschleiß mindern, wenn harmonieren (Abb. 2.):

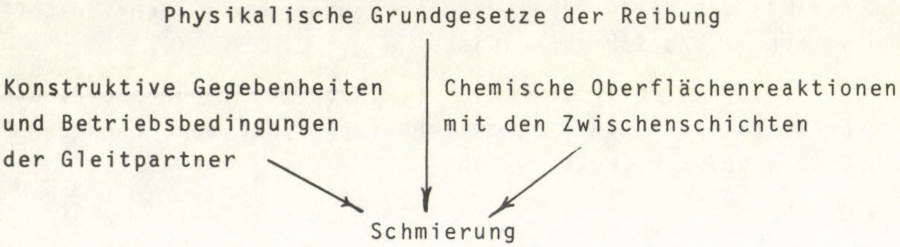

Abb. 2. Grundlagen der Schmierung

4. Aufstellung eines Stoffplanes

In der Tribologie ist die Aufstellung eines Stoffplanes und die Angleichung der Fachbegriffe besonders schwierig.

Wir haben in den Fächern Physik, Maschinenbau und Chemie verschiedene Fachsprachen, sehr oft sogar gleiche Fachworte, jedoch mit unterschiedlicher Bedeutung in diesen Fächern. Wir haben auch leider absolut falsche Begriffe in Benutzung.

Man muß die mehrdeutigen Begriffe in einen einheitlichen Stoffplan bringen und dann können wir uns für die Festlegung eines Begriffes entscheiden, wobei wir sehr oft zwischen mehreren Begriffen wählen müssen.

Der folgende Stoffplan wurde mit der Erfahrung aus ständigen Vorlesungen an der Universität Stuttgart seit Winter 1960 aufgebaut und enthält auch die Erfahrungen einer 15 jährigen Tätigkeit in der Praxis.

Nachfolgend werden die 8 Hauptteile der Tribologie stichwortartig beschrieben.

5. Die Hauptteile der Tribologie

Die Gesetzmäßigkeiten der Tribologie sind in Physik, Konstruktion und Chemie verankert. Hierauf hat jede Gliederung Rücksicht zu nehmen.

Die im 1. Hauptteil behandelte "Einführung in die Tribologie" zeigt die nachfolgend zusammengestellten Kapitel dieses Hauptabschnittes.

Im Hauptteil 2 müssen logischerweise zuerst alle "Tribologischen Grundvorgänge" behandelt werden.

Der ersten wichtigen Folgerung der Reibungsgesetze, den "Tribologischen Gesichtspunkten, Erfordernissen und Konsequenzen bei der Maschinenkonstruktion", ist der 3 Hauptteil gewidment.

Die technische Optimierung der gewollten Reibung ist Inhalt des 4. Hauptteiles "Tribotechnik". Technik ist die Perfektionierung gesicherter Zusammenhänge. Demgemäß bedeutet "Tribotechnik" Reibtechnik und beinhaltet die Perfektionierung gesicherter Reibvorgänge.

Die andere wichtige Folgerung nach der Tribotechnik faßt man mit dem Wort "Schmierung" zusammen. Ihre Definition und ihre Grundvorgänge sind bereits im Hauptteil 2 behandelt worden. Wir können also auf diesen Grundlagen aufbauen.

Danach haben wir als obersten Begriff "Schmierung", der sich in drei Teile, Schmierstoffe, Schmiertechnik und Schmierpraxis gliedert. Ihre Einzelheiten werden in Hauptteil 5-7 erläutert.

Ist ein Problem lückenlos geklärt, lassen sich auch alle komplexen Erscheinungen in Ursache und Wirkung eines oder mehrerer Einzelvorgänge aufteilen und in zahlenmäßig festlegbaren Grenzwerten formulieren. Meist nennt man diese Zahlenwerte "Anforderungsvorschriften". Ihrer Zusammenfassung ist Hauptteil 8 gewidmet.

1. Einführung in die Tribologie
2. Tribologische Grundvorgänge
3. Tribologische Gesichtspunkte, Erfordernisse und Konsequenzen bei der Maschinenkonstruktion
4. Tribotechnik
5. Schmierstoffe
6. Schmiertechnik
7. Schmierpraxis
8. Anforderungsvorschriften

Abb. 3. Hauptteile der Tribologie

6. Erläuterungen zu Hauptteil 1: Einführung in die Tribologie

Hauptteil 1 soll in die Tribologie einführen (Abb. 4.). Mit der Schilderung der Situation die Stellung der Tribologie in der Wirtschaft fixieren, soll den nachdrückenden Fachleuten gezeigt werden, wie in der Vergangenheit durch uneinheitliches und unsys-

1.1 Grundlagen
  1.1.1 Situation
  1.1.2 Terminologie (Erläuterungen)
  1.1.3 Definitionen (Erläuterungen)
1.2 Stoffplan
  1.2.1 Erläuterungen
  1.2.2 Definition: "Tribologie"
  1.2.3 Die 8 Hauptteile (HT) der Tribologie
  1.2.4 Erläuterungen zu HT 1-8
1.3 Stellung der Tribologie in der Wirtschaft
  1.3.1 Die volkswirtschaftliche Bedeutung der Tribologie und der Schmierung
  1.3.2 Privatwirtschaftliche Gesichtspunkte
  1.3.3 Unterschiedliche Interessen dreier Industriegruppen
  1.3.4 Psychologische Momente und weitere erschwerende Gesichtspunkte
  1.3.5 Berufsbild
  1.3.6 Ausbildung

Abb. 4. Hauptteil 1 der Tribologie: Einführung in die Tribologie tematisches Forschen - nebeneinander in zahlreichen Spezialgebieten - durch Vorurteile, Fehleinschätzungen und Fehler optimale Lösungen der Probleme nicht erreicht werden konnten, und wie es in der Zukunft besser gemacht werden kann.

7. Erläuterung zu Hauptteil 2: Tribologische Grundvorgänge

Der Hauptteil 2 "Tribologische Grundvorgänge" gliedert sich (abgesehen von den "Erläuterungen") in 6 Teile, weil 6 Erscheinungen im tribologischen Geschehen sich so voneinander unterscheiden, daß eine getrennte Betrachtungsweise zweckmäßig ist (Abb. 5.).

2.0 Erläuterungen
2.1 Reibung
2.2 Verschleiß
2.3 Gleitflächenschäden
2.4 Weitere tribophysikalische Erscheinungen
2.5 Tribochemische Erscheinungen
2.6 Schmierung, Definition

Abb. 5. Hauptteil 2 der Tribologie: Tribologische Grundvorgänge

In 2.1 bis 2.3 werden die fundamentalen Erscheinungen, Reibung, Verschleiß und Gleitflächenschäden behandelt. In Teil 2.4 und 2.5 sind die physikalischen Erscheinungen bzw. chemischen Umwandlungen zusammengefasst, deren Ursachen ausschließlich oder vorwiegend Reibvorgänge sind.

Im Hauptteil 2 "Tribologische Grundvorgänge" werden nur die grundlegenden Begriffsdefinitionen für Schmierung gegeben, Einzelheiten werden in den Hauptteilen 5, 6 und 7 erläutert.

7.1 Reibung

Der Teil 2.1 der Tribologie "Reibung" gliedert sich in 8 Kapitel (Abb. 6.):

2.1.1 Begriffe
2.1.2 Festkörperreibung = Kontaktreibung ohne Grenzschicht ("Trockenreibung")
2.1.3 Festkörper (Kontakt)-Reibung mit Grenzschicht ("Grenzreibung")
2.1.4 Innere Reibung einer Flüssigkeit, Viskosität
2.1.5 Flüssigkeitsreibung
2.1.6 Mischreibung
2.1.7 Messung der Reibung
2.1.8 Geschichtliches

Abb. 6. Teil 2.1 der Tribologie: Reibung

Leider gibt es für diesen fundamentalen Begriff noch keine eindeutige Begriffbestimmung. Ein Beispiel möge dies erläutern:

Die Ingenieurwissenschaft kennt 3 Reibungszustände: Festkörperreibung, Mischreibung und Flüssigkeitsreibung. Und diese Begriffe sind genormt. Die Mineralölwissenschaft kennt 4 Reibungszustände: Festkörperreibung, Grenzreibung, Mischreibung und Flüssigkeitsreibung.

Ich unterscheide 5 verschiedene Reibungszustände:

a) Festkörperreibung, das ist eine Kontaktreibung ohne Grenzschicht (Trockenreibung).

b) Kontaktreibung mit ungewollten Zwischenmedien, was mit "Technischer Trockenreibung" bezeichnet werden könnte.

c) Kontaktreibung mit gewollter Grenzschicht (Grenzschichtreibung oder Grenzreibung).

d) Mischreibung.

e) Flüssigkeitsreibung.

Es erscheint mir notwendig, den Zustand b) gesondert zu nennen, um die große Zahl der Veröffentlichungen über Reibung und

Verschleiß richtig einordnen zu können. Bei den vielen gemessenen Reibungszahlen zwischen 0,1 und 1,0 hat es sich nähmlich um Kontaktreibung mit ungewollten Zwischenmedien und nicht um Festkörperreibung gehandelt. Bei Festkörperreibung liegen die Reibungszahlen meist über 1.

7.1.1 Begriffe der Reibung

Die Abb. 7. soll für das Kapitel 2.1.1 die notwendigen Abschnitte zeigen, da alle die wichtigsten Grundlagen für die Tribologie sind.

2.1.1.1 Reibung, ein Energiebegriff
2.1.1.2 Reibungsmechanismen
2.1.1.3 Reibungsbegriffe, physikalische Größen der Reibung
2.1.1.4 Reibungsarten
2.1.1.5 Reibungszustände
2.1.1.6 Reibungszahl, Reibungskoeffizient, Reibbeiwert
2.1.1.7 Grundgesetze der Reibung ungeschmierter Oberflächen (Coulomb'sche Gesetze)
2.1.1.8 Messung der Reibungszahl
2.1.1.9 Reibungszahl in Abhängigkeit von den Reibungszuständen (Stribeck-Kurven)
2.1.1.10 Allgemeine Stribeck-Kurve
2.1.1.11 Erwünschte Reibung

Abb. 7. Kapitel 2.1.1 der Tribologie: Reibung, Begriffe

Wir müssen eindeutige Definition für die "Reibung, Reibungsmechanismen, Reibungsbegriffe und physikalischen Größen der Reibung, Reibungsarten, Reibungszustände und Maßzahlen für die Reibung einschließlich deren Messung" haben. Daß an dieser Stelle die bekannte "Stribeck-Kurve" behandelt werden muß, ergibt sich von selbst.

7.2 Verschleiß

Beim Grundvorgang "Verschleiß" beschränke ich mich auf die Definition. Die entscheidenden Worte sind hervorgehoben. Unter

"Verschleiß" soll also unerwünschte Lostrennung von Werkstoffteilchen an den Oberflächen durch physikalische und chemische Vorgänge verstanden werden.

7.3 Schmierung

Das Gebiet der Schmierung berührt alle Gebiete der Technik.

Schmierung ist in der Praxis die im Maschinenwesen unumgängliche Aufgabe, alle tribologischen Erscheinungen im Maschinenbetrieb auf zulässige Größen zu reduzieren.

Immer, wenn zwei sich berührende materielle Flächen eine Relativbewegung haben, müssen wir deutlich zwischen Reibung, Verschleiß, Verschweißen bzw. Oberflächenschäden unterscheiden. Diese drei Begriffe beinhalten aber einander. Fest steht, daß der Grundvorgang im mikrophysikalischen Bereich die Reibung bzw. die ausreichende oder nicht ausreichende Reibungsminderung ist und daß alle anderen Vorgänge und Erscheinungsformen, wegen der Überschreitung bestimmter Beanspruchungsspitzen, Folgeerscheinungen sind, deshalb im makrophysikalischen Bereich alle drei Auswirkungen nicht konform und erst recht nicht proportional verlaufen müssen.

Eine vollständige Definition mit allen notwendigen und hinreichenden Formulierungen lautet: Schmierung im technischen Sinne bei sich berührenden festen Stoffen, die sich mit - nach Größe und/oder Richtung - unterschiedlichen Geschwindigkeiten bewegen, durch eine feste, flüssige oder gasförmige Zwischenschicht, die entweder durch mechanische Zuführung und/oder chemische Umwandlung an den Oberflächen zur Wirkung kommt, den Kontakt der Oberflächenrauhigkeitsspitzen zu verringern oder zu verhindern, und als Folgeerscheinung Reibung, Verschleiß und Oberflächenschäden zu mindern.

8. Erläuterungen zu Hauptteil 3: Tribologische Gesichtspunkte, Erfordernisse und Konsequenze bei der Maschinenkonstruktion

Dieser wichtige Hauptteil Lehandelt die tribologischen Gesichtspunkte bei der Maschinenkonstruktion, deren Erfordernisse bereits bei der Maschinenkonstruktion Konsequenzen haben. Oft werden letztere nicht in ausreichender Weise berücksichtigt.

9. Erläuterung zu Hauptteil 4: Tribotechnik

Die Tribotechnik ist ein Hauptteil der Tribologie.

Die Unterteilung zeigt einige wichtige Teilgebiete aus dem Maschinenwesen (Abb.8) bei denen Reibung eine mechanische Notwendigkeit ist.

4.1 Reibung als mechanische Notwendigkeit
4.2 Umformtechnik
4.3 Fördertechnik
4.4 Schienenfahrzeuge
4.5 Bremsen
4.6 Reibkupplungen
4.7 Synchronisationen
4.8 Haften, Kitten, Kleben

Abb. 8. Hauptteil 4 der Tribologie: Tribotechnik

Der derzeitige Gebrauch des Wortes "Tribotechnik" im Sinne von Schmiertechnik ist ein Wortmißbrauch und sollte nicht weiter in die Fachliteratur eingehen. "Tribotechnik" heißt in seiner Übersetzung ganz einfach "Reibtechnik".

10. Erläuterungen zu den Hauptteilen 5, 6, 7 Schmierstoffe, Schmiertechnik, Schmierpraxis

In den Oberbegriff Schmierung lassen sich alle Vorgänge und Probleme zwanglos einordnen, wenn man die drei Begriffe, Schmierstoffe, Schmiertechnik und Schmierpraxis unterscheidet. Wie sich diese Begriffe voneinander abgrenzen, geht aus der weiteren Unterteilung dieser Hauptteile hervor.

10.1 Hauptteil 5: Schmierstoffe

Ehe man Schmiertechniken und Schmierpraktiken studieren kann, muß man selbstverständlich die Schmierstoffe genau kennengelernt haben.

Die Abb. 9 soll für den Hauptteil 5 die notwendigen Teile zeigen.

5.0 Allgemeingeltendes
5.1 Rohstoff für Schmierstoffe
5.2 Verarbeitung der Rohstoffe
5.3 Versorgung mit Schmierstoffen
5.4 Zusammensetzung und chemische Konstitution
5.5 Primärzustände
5.6 Zusätze bzw. Additive
5.7 Primäreigenschaften
5.8 Spezialeigenschaften und Stoffe für spezielle Zwecke
5.9 Definierte Prüfverfahren und ihre Aussagekraft (Kennwerte)
5.10 Technologische Prüfverfahren

Abb. 9. Hauptteil 5 der Tribologie: Schmierstoffe

Die Teile 5.1 bis 5.6 behandeln die Herstellung der Schmierstoffe. Wichtig erscheinen mir die Begriffe "Primärzustände" (5.5) und "Primäreigenschaften" (5.7). Durch diese Begriffe sollen die für alle Schmierstoffe wichtigen Eigenschaften und Aggregatzustände hervorgehoben und von Spezialeigenschaften abgegrenzt werden.

Mit den Teilen 5.9 und 5.10 endet Hauptteil 5 "Schmierstoffe", da es das Höchsterreichbare für einen Stoff ist, wenn viele oder manchmal auch alle seiner Eigenschaften durch Kenngröße und ihre Zahlenwerte charakterisiert werden können.

10.1.1 Überblick über die wesentlichen Aufgaben und Eigenschaften der Schmierstoffe

Die wesentliche Funktion eines Schmierstoffes besteht gemäß der Definition für Schmierung darin, die reibenden Oberflächen voneinander zu trennen und auf diese Weise Reibung, d.h. Energieverluste und Verschleiß herabzusetzen. Zusätzliche Funktionen, die unter bestimmten Bedingungen von großer Bedeutung sein können, sind die Abführung der Wärme, der Schutz der Metalloberflächen gegen Korrosion und Abdichten.

Je nach Einsetzzweck sind 46 Aufgaben zu beachten (Abb. 10). Obwohl die Schmierstoffe für viele Anwendungen geeignet sind, besitzen sie doch Grenzen in der Hinsicht der Belastungsfähigkeit und des Widerstandes gegen Erwärmung und chemischen Angriffen.

10.2 Hauptteil 6: Schmiertechnik

Schmiertechnik hat die Aufgabe, mit kleinstem Aufwand eine optimale Reibungsminderung und Verschleißminderung zu erreichen. Es muß eine optimale und nicht maximale Reibungsminderung angestrebt werden, da in vielen Fällen eine hohe Reibung oder ein Rest von Reibung gewünscht ist, wie es die Vorgänge gehen, Schleifen, Bremsen usw. zeigen.

Was alles bei der Verbesserung der Schmiertechnik beachtet werden muß, zeigt sich am besten durch einen Überblick über die zahlreichen Einflußgrößen des Schmiervorganges (Abb. 11).

Zusammenfassend sei gesagt: Es müssen immer alle Einflußgrößen, alle Anforderungen und alle Eigenschaften berücksichtigt werden.

10.3 Hauptteil 7: Schmierpraxis

Im Hauptteil 7 erfolgt die weitere Unterteilung nach Maschinenelementen, d.h. nach Schmierstellen (Abb. 12).

1. Reibung
    2. Statischer Reibwert
    3. Dynamischer Reibwert
    4. Reibwertänderung mit Temperatur
    5. Reibungsminderung
6. Verschleiß
    7. Verschleißminderung
    8. Verschleißsteigerung (Einlaufen)
9. Ölfilmzerreißfestigkeit
10. Ölfilmhaftfähigkeit
    11. Benetzungsvermögen
    12. Grenzflächenspannung
13. Kompressibilität
14. Angepasste Viskosität

    Geringe Viskositätsänderung durch
    15. Temperatur (Visk.-Index)
    16. Druck
    17. Oxidation
    18. Fremdstoffe
    19. Wasser
    20. Kraftstoff
21. Kälteverhalten
22. Stockpunktsenkung
23. Oxidationsverzögerung
24. Thermische Stabilität
25. Verträglichkeit mit Metallen
26. Korrosionsschutz
27. Rostschutz
28. Wasserabweisen
29. Emulsionsbildung
30. Schaumverhalten
    31. Schaumneigung
    32. Schaumstabilität
33. Verträglichkeit mit Dichtungswerkstoffen
34. Dispergierwirkung bzw. Verteilungsvermögen
35. Reinungs- (Detergent-) Wirkung
36. Schlammverminderung
37. Neutralisation
38. Kühlwirkung
39. Dichtwirkung
40. Geräuschdämpfung
41. Verträglichkeit mit gleichen Produkttypen
42. Lagerfähigkeit
43. Farbe
44. Geruchsverbesserung
45. Keine Gesundheitsschädigung
46. Keine Giftwirkung

Abb. 10. Aufgaben und Eigenschaften moderner Schmieröle

1. Schmierstelle bzw. konstruktive Gegebenheiten
    - Gleitbahnen, Gleitlager
    - Wälzlager, Getriebe
    - Oberflächenbeschaffenheit
    - Lagerspiel
    - Thermische und mechanische Veränderung der Konstruktionsteile
2. Bewegungsbedingungen
    - Drehgeschwindigkeit
    - Gleitanteil
    - Last bzw. Flächendruck
    - Temperatur in der Schmierstelle
    - Temperatur um die Schmierstelle
3. Werkstoffe bzw. Werkstoffpaarungen
    - Elastische Verformungsgrenzen
    - Plastische Verformungsgrenzen
    - Bruchfestigkeit
4. Schmierstoffe
    - Haupteigenschaften:
        - Viskosität
        - Temperaturabhängige Viskositätsänderung
        - Druckabhängige Viskositätsänderung
        - Haftfähigkeit
        - Reibungsminderung
        - Verschleißschutz
        - Ölfilmbelastbarkeit
    - Nebeneigenschaften:
        - Thermische Stabilität
        - Oxidative Stabilität
        - Keine schädigenden chem. Angriffe auf Eisenmetalle
        - Keine schädigenden chem. Angriffe auf Nichteisenmetalle
        - Neutralisation saurer Verbindungen
        - Dispergiervermögen fester Fremdstoffe
        - Wasch- (Detergent-) Wirkung
        - Kälteverhalten
        - Schaumneigung, Schaumstabilität
        - Verträglichkeit mit Dichtungsmaterial
        - Kühl- und Dichtwirkung

Abb. 11. Einflußgrößen des Schmiervorganges

7.0 Allgemeingeltende Schmierpraktiken
7.1 Schmiervorgänge bei Bearbeitungsprozessen
7.2 Schmiervorgänge an Maschinenelementen
7.3 Schmiervorgänge in Kraftmaschinen
7.4 Schmiervorgänge bei Arbeitsmaschinen
7.5 Kombinierte Schmiervorgänge bei Maschinen und Anlagen

Abb. 12. Hauptteil 7 der Tribologie: Schmierpraxis

11. Erläuterung zu Hauptteil 8: Anforderungsvorschriften

Den Anforderungsvorschriften wurde ein eigener Hauptteil gegeben, um zu dokumentieren, daß die einwandfreien und ausreichend formulierten Anforderungsvorschriften eine Zusammenfassung aller in den vorangegangenen Hauptteilen behandelten Probleme ist.

Anforderungsvorschriften sind die eindeutige und ausreichende Formulierung für die tribologischen Grundvorgänge, Primärzustände und Primäreigenschaften der Schmierstoffe und für die speziellen schmiertechnischen Erfordnisse im Maschinenbetrieb.

ZUSAMMENFASSUNG (Abb. 13)

Die Tribologie baut als Grundlage auf den Forschungsergebnissen in Physik, Ingenieurwissenschaft und Chemie auf.

Der durch die tribologischen Gesetzmäßigkeiten bzw. die physikalischen Reibungsgesetze erkannte Schmierzustand und die durch die konstruktiven Gegebenheiten bei der Maschinenherstellung entstandene Schmierstelle erfordern:

a) in der Schmiertechnik das Anpassen der Schmierstoffe, wie sie gemäß den notwendigen chemischen Oberflächenreaktionen in der Mineralölindustrie hergestellt werden, and das gemäß den Betriebsbedingungen ausgewählte Schmiersystem.

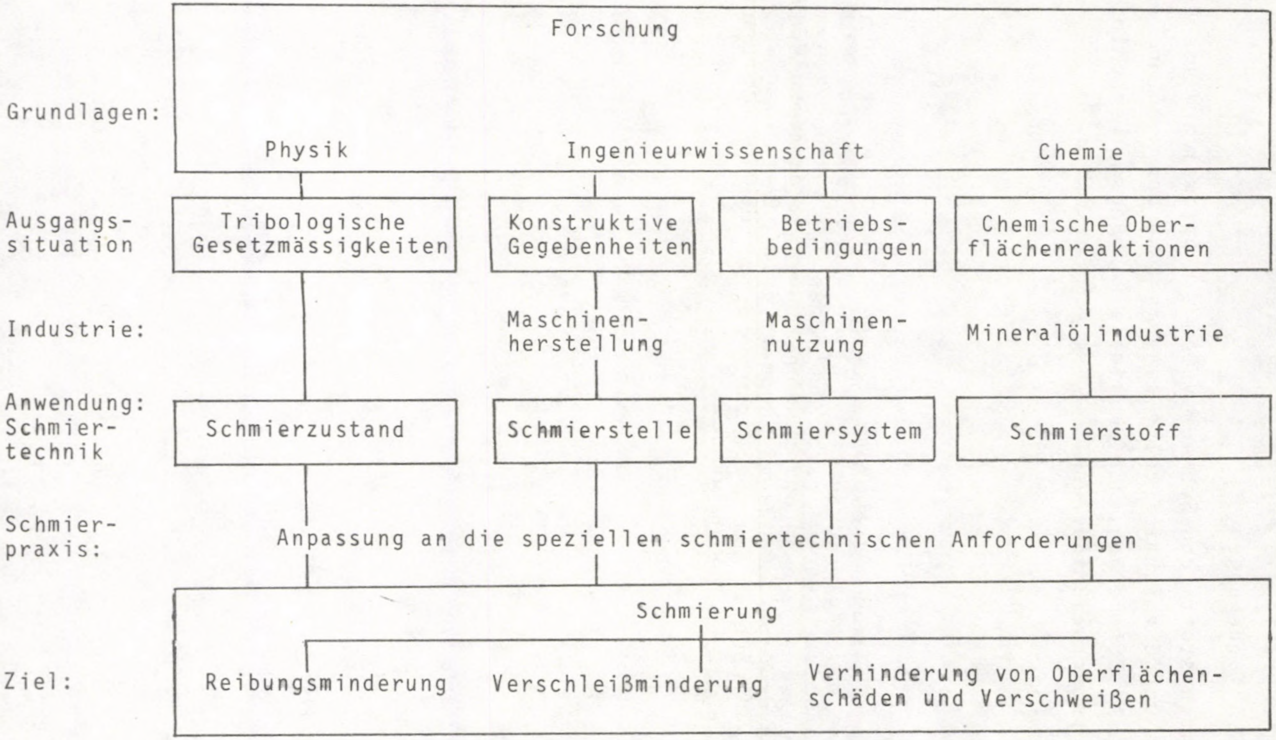

Abb. 13. Tribologie

b) in der Schmierpraxis die Anpassung an die speziellen schmiertechnischen Anforderungen.

Wenn Schmierstoff und Schmiersystem in optimaler Weise dem Schmierzustand und der Schmierstelle angepasst werden konnten, haben wir die beste Schmierung, d.h. maximale Reibungs-, Verschleißminderung und Verschweißhinderung.

РЕЗЮМЕ

Области, в которых работали физики, химики и механики за много десятилетий, стали областями науки и специалистов. Такая область специалистов и науки - это трибология. Появление трибологии дает все больше значения обобщенному пониманию разделов и названий, терминологий трибологии для специалистов разных стран.

Настоящая работа дает осведомление о науке трибологии и предложения для общего понимания ее.

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APPLICATION OF COMPUTER TECHNIQUES

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The author discusses the theoretical aspects of the application of computer techniques, and compares the three generations of the computers so far produced with the three development stages of programmes and assignments. Examples of the latter are taken from the chemical industry. The author establishes that the most important condition for the increased application of computers in Hungary is the improvement of the scientific research organisation in this field.

In order to implement the Computer Technology Programme, the state Economic Committee allocated a vast sum, which nearly equals, in magnitude, the total amount invested by any one single ministry within the 5-year development period. However, the thousands of millions set aside for the Computer Technology Programme are investment and budget allocations which do not produce new material benefits. Their significance is of a different nature, namely they extend the knowledge of computer techniques and, therefore, have an indirect effect on science and material production.

In this report, the intention is to proceed with a discussion that keeps the afore-mentioned facts in mind. In his daily work, a chemist uses a variety of instruments, from the burette to the mass spectrometer, and - today - the electronic computer is increasingly becoming a very important member of the above group of instruments. When a burette or mass spectrometer is used in everyday work, the user acquainted with its operation, at least, in its essential outlines. If the electronic computer is considered a member of the above group of instruments, it therefore follows that the user should be familiar with its operation, at least in its general features.

The characteristic feature of an electronic computer is that it is able to solve, in a very short time, extremely simple arithmetical and logical problems. By reducing a complicated problem, say, a system of partial differential equations or a complicated logical problem into a series of simple mathematical operations, the electronic computer then becomes a handy tool for solving these complex problems. The process of breaking down the problem into simple operations is termed programming. A programme is a sequence of statements which can be interpreted and carried out by the computer. It is immediately clear that two topics are involved in this discussion, namely the one that concerns the tool - the hardware - whilst the other is connected with the various sequences of statements or programmes whose composition is, in all cases, the work of a human brain as it calls for the ingenuity of the programmer. Hence the collection of programmes is often termed software.

The Three Generations of Computers

The electronic computer was put into circulation in a commercial quantity about fiften years ago. Within this period, three successive generations of computers were invented. The first, second and third generation consisted of vacuum tubes, semi-conductors and integrated circuits respectively. The switch over from one generation to the other meant a decrease in the volume and weight, as well as a decrease in the electrical power requirement for the electronic computer. At the same time, the safety and speed of operation and the operative memory of the computer improved from generation to generation. The operative memory stores up the basic problems, the intermediary and final results, as well as the programme. In this way the computer became increasingly suitable for solving complex problems. In the third generation, new possibilities were incorporated. The inclusion of a further set of terminals, i.e. data input and output units did not represent a basic innovation of the computer, even though the former can be placed some kilometres away from the latter. The new features, however, were the development of time-sharing computers which can solve many problems simultaneously and the various methods of connecting two or more computers. The fourth generation of computers will consist of integrated microcircuits and this brand of computers is expected to predominate in the next decade.The fourth generation computers will presumably be miniature in size, so much so that a computer built from integrated microcircuits - having a capacity equal to that of the largest today - will hardly be bigger than the Hunor desk-top calculator. However, it would be misleading to suppose that this type of computer will eventually reach the desk of a chemist. This is because the price will probably be exorbitant and what is more, the central unit is by no means everything.

The central unit is connected to the peripherial units, i.e. the data storage, input and output units. The latter units provide the connection between machine and man. The miniaturization of the peripherial units is not so feasible, but here the generations are also distinguishable. The output units provide a perfect example. The output units of the first, second and third generation computers were a typewriter, a line printer and an optical unit respectively. Today, each and every one of these output units has its own specified field of application. Perhaps the reader has observed from the foregoing, the obvious necessity for more fundamental and technical research which is required to develop the man-to-machine connection. Studies carried out along this line showed that an extensive knowledge of computer techniques will lead to structures similar to that of telephone or engine telegraph. Furthermore, the possibility of interweaving them together cannot be excluded due to the telecommunications problems related to data processing.

The Three Generations of Programmes

The development of software or programming techniques took place in the phenomenal three-generation pattern distinguishable in the evolution of hardware and the machine-to-man relationship. For the first computers, the programme was formulated by breaking down the problem to fundamental steps, each of which was represented by a code, depending on the construction of the machine, and this code shows what the step stands for. Such programmes were said to be written in machine codes. The formulation of programmes in machine codes is not too difficult a task, but it cannot be called pleasant. Hence when the second generation computers first appeared,to which the actual "demographic explosion" in computers is attributed, the so-called programming languages were invented. In examining the syntaxes of programmes written in machine codes, it was found that some portions of the programmes are often repeated and if each of these repeated sections were defined as one unit, then the calculation steps could be written in units of higher order. In this way, programming would be easier and more amusing.The programme thus obtained cannot be interpreted directly by the computer, only with the help of a compiler programme which so to speak translates it into an intelligible machine language. About a dozen such languages have been invented within the last decade. These languages can be divided into two groups, namely the process-oriented and the problem-oriented languages. The languages of the former group are used in solving technical and scientific problems, whereas those belonging to the latter group are suitable for solving data processing (say statistical, and accounting,etc.) problems.

An unprecedented number of various programmes were formulated, as more and more second-generation computers were devised. At first, everybody wrote their own programmes, but as time went on, this method proved to be unsuitable.A far more advantageous method consists of adopting, whenever necessary, an already existing programme devised for a given type of problem. Thus programme libraries were established by computer-manufacturing companies and computer technique institutes. It was soon discovered that a number of programmes had already been formulated for the same problem.

Take for example the solution to a system of differential equations. Various numerical methods for solving this mathematical problem have been developed in mathematics. If, say, a reaction kineticist wishes to solve a system of differential equations obtained in the course of his kinetic studies, all he has to do is decide which of the programmes already worked out by others is more suitable to his purpose. Such a decision is not as easy to make as it sounds,for the most suitable method of solution usually depends on the nature and parameters of the problem. It is therefore more practical to somehow store all the programmes in packages. Every programme package has the same input and output structure, and it is up to the user to state shich of the existing methods of calculation is most applicable to his problem, or if he wishes to apply more methods, he should specify the order in which he intends to use them.

There is another type of programme package in which programmes of solutions to different problems are contained. The reason for packaging the various programmes together is that there is a constant demand for them and they can easily be used successively. For instance, a chemist could certainly use a programme package that would enable him to estimate the physical properties of chemical compounds.

The so-called system of programmes is the most noble of all types of software and was developed for the third-generation computers. The system of programmes is a collection of programmes or programme packages, whereby the data (or some of the data) calculated with the help of one programme can serve as the input data for the succeeding programme. The transfer of data from one programme to another within a given system may, depending on the circumstances and demands, take place entirely automatically or may require the dicision or intervention (or interaction) of the programmer. The condition for the interactive intervention is ensured by a suitable machine-to-man relationship.

The Three Categories of Problems

The software is the result of human endeavour and it is perhaps worthwhile to consider the human factor in the form of the man-to-man relationship, in other words, the manner in which this relationship takes shape with regard to a change in the nature of the problems. The computation problems may be divided, according to their complexity, into the following three categories (which more or less correspond to the software generations): individual calculations, combined computations and the calculations involving systems. These are the three categories that came into being and which still exist side by side. For individual calculations, the programme is formulated by a single person, who may be a chemist or some other specialist, and aims at performing individual calculations connected with his work.

The situation is different in the case of combined calculations. Here, co-operation between four men is required: a specialist in charge of the model of a physical, chemical, economic or other phenomenon; a mathematician who considers the mathematical side of the model and provides the method of computation which leads to the solution of the mathematical problem derived from the model. This is followed by the work of the programmer, who formulates the programme, in accordance with the rules of computer programming, from the algorithm provided by the mathematician and finally the coder puts in the finishing touches to the last detail. However, the role of the programmer should be stressed. There are many ways of programming the algorithm and to a large extent this determines the length of time required for the calculation. Our programmers transformed a programme several times in four years from the programme library prototype which we frequently applied. By leaving the original algorithm intact and making computer technique corrections, the speed of the calculation was improved. This example shows that programming can correctly be considered to be an independent profession. Such a group of people of various profession. Such a group of people of various professions and experience mentioned in the foregoing is often called a team, whose task is to prepare a programme for combined calculations. In the case of individual calculations, therefore, the formulation of the programme depends on the extensive experience and professional knowledge of the single specialist, whilst for combined calculation of the programme depends on the nature of the co-operation developed among the various specialists, in addition to their professional knowledge.

I have mentioned that extensive systems of programmes are also developed. In this instance a new type of technique took shape which is connected with the man-to-man relationship. This type of work is begun by analyzing the system, whereby the elements of the system are determined and the manner in which the elements are related to another. The system analysis is the job of the systems engineer who, consequently, composes the general model of the entire system on the basis of the analysis results and finally entrusts the elaboration of the system's elements to the appropriate teams. This is a typical example of hierachically organised activity. In the case of combined calculations, the co-operation within the given team illustrates the man-to-man relationship. In preparing the systems of programmes connected with the calculations of extensive systems, a scientific work-organisation represents and brings about the man-to-man relationships needed for the development of a system of programmes.

Some Examples in Chemistry

I proceed to illustrate the foregoing discussion with examples encountered in chemistry. An individual problem may be the following: the estimation of the chemical equilibrium of a multicomponent reaction. The solution to this problem does not require the co-operation of a programmer, simply because the linear programming technique would be sufficient for which programmes are available in any Hungarian computer institution. As an example of combined calculation, it should be mentioned that the A.I.Ch.E. composed a programme package for the estimation of the physical properties of compounds on the basis of structural formulae. This programme package can be used in estimating a considerable number of physical properties in terms of the state functions. The formulation of this programme package lasted three years and cost a total of $ 300,000. It was marketed on a magnetic tape at a price of $ 8,000 a piece. In Hungary no such computer was available, to which this programme package would be applicable and, therefore, the FISC programme package was worked out, which enabled us to estimate a narrower group of the physical properties, on the basis of such basic data of the materials as the critical temperature, critical volume, and normal boiling point, etc., (and not from the structural formula). The FISC programme package involves about 200 materials. The third example concerns the system of programmes and in this instance the SIMUL system is cited. The SIMUL was developed by a team of 50 Hungarian specialists, in co-operation with one another, for the mathematical simulation of complex unit operations (entire production lines). The SIMUL system applies the FISC programme package, mentioned in the foregoing discussion, for the estimation of physical properties. It is important to emphasize the fact that the use of the SIMUL system does not require a knowledge of programming. It is sufficient to know a number of concepts and rules of programming, with the help of which, the problem can be formulated. In this manner, the SIMUL system is brought into action, whereby it automatically performs the required calculations and prints the results. Here, a programming language is also involved in which such concepts as distillation, heat exchanger, reactor, and recirculation, etc., are used. The latter correspond to those concepts of chemical technology which can be interpreted by the SIMUL system. The practical importance of the development and application of such simulation languages is definitely evident.

The Problems of Increasing the Knowledge of Computer Techniques

In the foregoing discussion, I placed special emphasis on the importance of software in the application of computer techniques. Indeed, the chemist is very closely associated with the hardware units, but the mentioned amphasis is justified by a general and important experience. Most people presume that in order to extend the knowledge of computer techniques, all the state has to do is set aside a certain amount of funds for a specified number of years and obtain the necessary number of computers. Computers, in a similar manner to any other machine, can achieve nothing on their own and so have to be handled by the professional personnel. The implementation of the Computer Technology Programme will yield the expected scientific, technical and economic results only if timely and basic preparations are ensured, especially with regard to the composition of software material (i.e. widely applicable programmes). A variety of circumstances make this task difficult.

The knowledge of computer technology in a given country does not merely mean the number of people who have studied programming as a subject and who are capable of transfering the given information from one cell of the available computer to the other. One other aspect of computer technique involves the flow of information from every pool of the computer institution so that if anybody wished to use a computer technique he will know exactly which pool can provide him with a ready programme for the solution of his problem. The situation in Hungary is that there are at present very many different types of computers which means that a programme run on one computer cannot be transfered to another, without making the necessary corrections. Perhaps it would be more advantageous as a first step, to establish a software library centre, so as to know the number of programmes available in the country and consequently aim at developing a unified computer technique system.

The Hungarian Academy of Sciences is responsible for the important research task, called "the applications of computer techniques". A major part of the topics proposed concerns the problems associated with software and requires a sound sense of proportion. In reality, hardware research is at most, performed to the limit of good and appreciable concepts in Hungary.We do not aim to carry out research work for the construction of commercial computers of our own, as the basic technical requirements cannot be met. It may however be visualized in the field of an integrated research programme. But the proposed topics of research do not refer to such a possibility.

The proposed research topics - although they are considered to be realizable - will not be an easy task, presuming that the usual methods of research administration and direction are maintained. For the research directive to remain alive and blooming, it is necessary to establish a body that possesses the necessary authority, worthy of the importance of the topic and the expense associated with it. This body would then perform its duty on a solid computer technology basis. The Academy is already in possession of the necessary hardware. Whether it will be able to compose the software is, of course, another matter. This may in itself be a research topic and may therefore deserve the attention of the research directive, constituting a part of the latter. If an administrative body were formed for this research directive, within the Academy the latter would have to acknowledge that the increased application of computer technology demands some amount of stimulation. Its extension has sociological and psychological repercussions, which may be accelerating or decelerating in nature. My feeling is that at present the latter effects prevail.

РЕЗЮМЕ

Автор занимается теоретическими вопросами применения вычислительной техники. Сопоставляет три до сих пор произведенных генераций ЭВМ с тремя ступенями развития. Изложенное дополняет наглядными примерами из области химической промышленности. Далее установлено автором, что в настоящее время самым важным условием распространения ЭВМ в Венгрии является повышение организованности научных исследований в этой области.

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THE APPLICATION OF NATURAL GAS AS A RAW MATERIAL FOR THE CHEMICAL INDUSTRY AND THE DEVELOPMENT OF THIS BRANCH OF THE INDUSTRY SINCE WORLD WAR II.

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The author presents a review of the development of the Hungarian natural gas industry and the industrial application of natural gas. A detailed survey of the research work carried out in this field at the Hungarian Oil and Gas Research Institute since 1950 is given.

At first, the author deals with the experiments concerning the production of acetylene and synthesis gas by the partial oxidation of methane, starting with the theoretical background, and then goes on to discuss the experiments carried out at laboratory, pilot plant and plant levels. The successes achieved resulted in the production capacity of 2.5-3 tons of acetylene per reactor in the mid-1950s.

In the last 10-15 years, the Institute established a combustion laboratory, where almost all the important parameters can be determined. In addition, it played an important role in the development of the national natural gas industry, e.g. in the improvement of the adsorption process applied by the Répcelak Carbonic Acid Company and in the solution to the special problems connected with the change over from town gas to natural gas.

In 1948, when the MÁFKI was established, the "founding fathers" already thought of the application of natural gas in chemical engineering and this fact was emphasized by the obvious inclusion of the word "gas" in the name of the Institute.At the initial planning stages of the Institute, two departments, namely the Departments of Physical Chemistry and Organic Chemistry were already carrying out useful research-work. Undoubtedly, natural gas is very important in industry and the fact that Hungary alone produced 4,100 million Nm³ in 1972 makes it obvious. However, after this brief introduction of the historical background, it must be pointed out that the situation was very different during the years of reconstruction necessitated by the war damage. Indeed, the general public kept a sceptical eye on the efforts made at the time by our research-teams. Today, it is no exaggeration to state that time has proved that those people who believed in and struggled for the establishment of the Hungarian gas industry were correct in their assumptions. The table below illustrates the application of natural gas in Hungary.

Year	1960	1965	1971	1972	1975*
Nat.gas: 10^6 Nm^3	292	1,122	3,718	4,100	6,000

*Planned data + imported quantity

Referring again to the work carried out at the Institute, the actual experimental research started in January, 1950. After studying the work carried out prior to that, it was decided at the Institute to pay special attention, first and foremost, to the study and realization of the partial oxidation of methane.

It was clear from the minimal data available in literature that only 8 % of the methane under processing was lost in the form of carbon dioxide, the remainder being obtained in the form of acetylene and synthesis gas. Although the material and personnel requirements for the research-work were met, these were limited in comparison to the present level of the development of the national economy.

The earlier mentioned process essentially consisted of burning up the natural gas (methane) mixed with the least amount of oxygen possible (i.e. near the upper combustion limit) and then the gases were suddenly cooled down from 1,400 °C to 80 °C. The burner shaped in this manner ensures that the acetylene obtained does not decompose under an average residence time of 0.01 second.

The research-work was pursued simultaneously along both theoretical and experimental lines. Laboratory experiments were carried out in the autumn of 1950 at the Institute's experimental plant at Pét with a quartz burner whose dimensions agreed with those of the only nozzle of the plant burner system.

The pilot plant was ready within a very short time and in December, 1951 the first tests were carried out there. This plant was built for the partial oxidation of 50 Nm^3/hr of methane and produced 100 Nm^3/hr of gases. When methane or oxygen was preheated to 350 °C or 300 °C respectively, 7.8-8.3 % of acetylene was obtained. This pilot plant was built from such structural materials which were completely identical with those of the industrial plant to be installed. Thus, for example, the reactor had firestones consisting of 72 holes and water-cooled nozzles.

In addition to the preparation of the expected gases, the research-workers elaborated and delivered all the scientific and technical calculations necessary for industrial plant designing. This plant was realized in the sphere of Hungarian-Romanian economic co-operation between 1953-1957. It was designed by VEGYTERV and the investment was borne by the TKV. It is worth mentioning that the plant was designed for the processing of 2,000 Nm^3/hr of methane which surpassed the capacity of the then existing plant. Another important new feature was that the high-voltage Cotrell--Möller equipment applied in desooting the 3,800 Nm^3/hr of the gaseous products, ensured perfectly soot-free gases, which were directly passed on to the other plant section, where acetone was produced from acetylene by a catalytic hydration process developed at the Organic Chemical Department.

Depending to the experimenta conditions, the daily output of the plant was 2.5-3.0 tons. This was wholly converted to acetone, then the acetylene was absorbed from the gas and technical acetone was produced from the dilute acetone solution by batch and later continuous rectification. This was then considered to be a major achievement, as the petrochemical plants in Central Europe were still at the initial experimental stage. The plant was delivered to Romania in 1958.

From then on the research workers went on to study the development of partial oxidation, new, more economical combustion and thermal decomposition processes. Between 1961-1965, a flameless reactor operating under surface combustion was developed. Combustion took place on corundum particles coated with Pt catalyst. On the basis of the laboratory experiments a pilot plant with an output of 60 Nm^3/hr was built where experiments were performed under pressure (max. 3 atm) and a higher yield of acetylene was obtained than with the flame reactor.

One other important development of the partial oxidation involved some modification, whereby a portion of the gas produced, the "synthesis gas fraction", was fed back into the flame reactor after being mixed with the incoming methane. The research team also constructed new burners for use in the laboratory and the pilot plant. Among others, good results were obtained with "slit-burners". The required amount of oxygen and coking decreased.

During 1966-1967, the research team worked on the thermal decomposition of hydrocarbons heavier than methane. The aim of the experiments - at laboratory and pilot plant levels - on the decomposition of gasoline was simultaneously to prepare both ethylene and acetylene. With a gasoline feed of 50 kg/hr and no preheating, a yield of acetylene-ethylene of 40 wt % was obtained.

A review of another important application of natural gas now follows. It is well known that the sites of natural gas in Hungary, in most cases, contain gases rich in carbon dioxide, indeed, some contain hydrocarbons only as impurities compared to CO_2.

From 1959-1971, the Institute's Department of Physical Chemistry carried out wide-ranging studies on the adsorption cleaning system and the removal of impurities from carbon dioxide for the Répcelak Carbonic Acid Company. After developing a chromatographic method of analyzing the impurities with laboratory equipment at 50-60 atm. with various adsorbents, the optimum conditions for the adsorption were established. In co-operation with the designing institute, the experiments were continued at a plant level in 1966-1967. A close correlation between the laboratory and the plant results was obtained and an odourless carbon dioxide was produced.

To enchance the applicability of natural gas as town gas, wide-ranging studies were carried out at the Institute for the installation of natural gas transporting pipes in the capital. The MÁFKI worked on this problem in co-operation with the Budapest City Gas Works.

To perfect the network, two conditioning materials were developed which were introduced and are still in use.The compactness of the gas network is ensured by bitumen emulsion treatment, whose technology was developed at the Institute, on the basis of the circumstances prevailing in Hungary. This technology gained industrial application.

Considering the activities the Institute carried out in the industrial application of natural gas, it was considered that a balance should be drawn up of this work and that not only the successes, but also the difficulties should be mentioned. Today, it is clear that at the beginning, the necessary materials (such as heat-resisting steel) and personnel were not available, which would have made it possible to simultaneously solve the extensive problems. However, these difficulties made the research workers more conscientious of their assignment and gave rise to a special relationship between them, whereby they helped one another. All this resulted in the accumulation of theoretical and practical knowledge, which proved to be extremely useful in carrying out such assignments as the installation of the acetylene plant at the Borsod Chemical Combine and the initiation of other new plants.

Another practical result was that a new laboratory was established at the Institute, where all types of combustion studies and measurements could be carried out, and combustion studies of any type of gas could be made.

The natural gas industry has always been dynamic and will always remain so, as far as we can predict. The acknowledgement of this dynamic nature makes it necessary to ensure that in the future the research work keeps pace with the requirements of our times and with the interests of the national economy. The MÁFKI will undoubtedly look forward to more successes in the coming decades.

РЕЗЮМЕ

Автор в начале дает обзор о развитии производства природного газа Венгрии в целом, далее осведомляет об использовании природного газа в химической промышленности. В рамках этого он подробнее обсуждает исследовательские работы, направленные по этому вопросу и проведенные с 1950 года в Венгерском Научно-Исследовательском Институте Нефти и Природного Газа.

Автором изложены опыты по получению синтезного газа и ацетилена путем парциального окисления метана, выполненные в теоретическом, лабораторном, опытно-заводском и наконец в производственном масштабах. Достигнутые результаты дали возможность получить 2,5-3 тонны в сутки ацетилена в одном реакторе уже в середине 1950-х годов.

За последние 10-15 лет Институтом была создана лаборатория для изучения процесса сгорания, в которой можно определить любой важный параметр. Институт кроме этого содействовал в дальнейшем развитии отечественной промышленности природного газа, так например участвовал в улучшении адсорбционного процесса у Предприятия производства углекислого газа в Репцелак, или в решении специальных вопросов, возникших при перестройке на природный газ с бытового.

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PROBLEMS OF SECURING MONOMERS FOR THE PRODUCTION OF CIS-ISO-POLYISOBUTYLENE CAOUTCHOUC

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In the mid-1950s, many processes using the modified Ziegler-Natta catalyst systems for the preparation of 1,4-cis-polyisoprene were developed. The elastomers thus obtained correspond to the natural caoutchoucs, but the difficulty of providing the required monomers slows down the production of elastomers. The problem arose from the fact that the price of the monomer is high, while that of the polymer is low, due to the relatively low price of natural caoutchouc.

If the price of natural caoutchouc were to rise, the situation might change, considering that a variety of processes for manufacturing isoprene have been developed, among which many have been realized.

The processes developed or realized can be divided into three groups:

1) Processes where ordinary C_5 hydrocarbons are applied.

2) Processes where the necessary C_5 hydrocarbons are synthesized from other hydrocarbons.

3) Processes based partly on hydrocarbons and partly on intermediary compounds containing oxygen.

The production of isoprene is considerably expensive. The cost of producing isoprene from C_5 fractions of pyrolysis gasoline is relatively low, but the problem with this process is that fairly large outputs of ethylene are needed to obtain the required quantity of C_5 fractions.

The conditions for a real boom in the production of cis-polyisoprene caoutchouc are as follows:

a) the price of caoutxhoucs should remain stable at a high level.

b) fields of application should be found for the by-products of the processes.

In the past two decades, with the advent of petrochemically based synthetics, plastics, synthetic fibres and synthetic caoutchoucs, significant progress has been made in the replacement of natural structural materials with synthetic ones. Figure 1 illustrates the application of elastomers.

On the basis of the limited available data, the total amount of caoutchouc applied in 1973 was 9 million tons, out of which 3.3 million tons was natural and 5.7 million tons was synthetic caoutchouc. It follows taht the increase in the application of the latter surpasses that of the former. The predicted 12-13 million tons of caoutchouc for 1980 is expected to consist of 7.5-8.5 million tons of synthetics, a proportion of nearly 66 %.

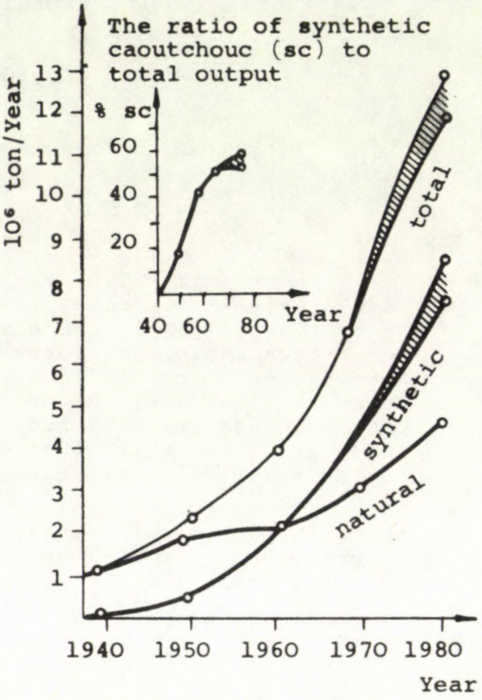


Fig. 1. The trend of world-wide application of caotchouc

According to earlier estimates for 1980, the output of natural caoutchouc was supposed to remain stable at 3 million tons a year, but the latest studies predict a further increase over and above that level.

Ever since the chemical composition of natural caoutchouc was determined in the first decade of this century, renewed efforts have frequently been made to produce and ensure the polymerisation of 2-methyl-1,3-butadiene. The latter was accomplished in the mid-fifties. With the help of modified Ziegler-Natta catalysts, many processes were developed for the preparation of 1,4--cis-polyisoprene. The elastomers obtained in this way more or less corresponded to the qualities of natural caoutchoucs, depending on the sic isomer content and, indeed, in some respects, they proved better than natural caoutchoucs.

However, the latter successes did not result in the rapid spread of cis-polyisoprene caoutchoucs. The difficulty of securing the monomers proved to be one of the most important impediments to polymer production.

The output of 1,4-cis-polyisoprene caoutchouc and the demand for isoprene monomer are illustrated by Table 1.

Table 1. The trend of the world wide demand for isoprene based on cis-polyisoprene production estimates

	Cis-polyisoprene outputs, 1,000 t/year			
	1970	1973	1975	1980
North America	140	160		
South America		40	500	700
Western Europe	70	195		
Africa, Asia, Australia		60		
C.M.E.A. countries	100	300	600	1,100
Total:	310	755	1,100	1,800
Total demand for iroprene	320	780	1,140	1,860

The table is based on the data of reports and articles of various sources. A part of these data turned out to be uncertain. For instance, the Bayer Company planned to establish a plant with an output of 80 thousand tons a year by 1975, but the latest reports indicate the postponement of the project. The situation is the same with regard to the isoprene-polyisoprene plans of France.

The problem arose from the simple fact that the production cost of the monomer is high, whereas the price of the polymerised product is low due to the relatively low price of natural caoutchouc. According to Dr. Engler, the Director of Bunawerke Hüls, a change in either of the said factors (i.e. if the monomer were to be cheaper or the caoutchouc were to be more expensive) woulr permit the rapid implementation of the various projects already designed for the preparation of isoprene caoutchoucs, some of which have actually been tested at an industrial level.

These processes can be grouped into three categories:

The first group can be said to involve the application of ordinary C_5 hydrocarbons (Figure 2).

This group includes the following:

a) Isoprene recovery from pyrolytic C_5 fractions by the various versions of extractive destillation (BASF-NMP, JSR-DMF, SHELL-ACN, SNAM-Morphylan).

b) Isoamylene recovery from cracked gasoline and the dehydrogenation of isoamylene (a combination of Acro-Stratford-Shell-Dow processes).

c) Two-stage dehydrogenation of isopentane (Soviet process).

d) One-stage dehydrogenation of isopentane (Houdry process).

The second group involves processes in which the C_5 chain of the appropriate configuration (2-methyl butane) is synthesized from other hydrocarbons (Figure 3).

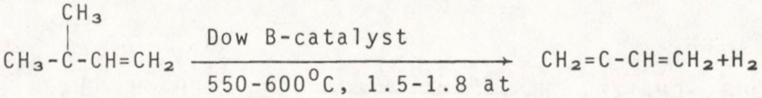
These include the following:

a) Goodyear-SD process in which the C_6 chain is produced by the dimerization of propylene and the consequent demethylation of the C_6 product results in a C_5 chain.

b) The different versions of the Phillips Triolein process, whereby isoamylene is produced by the disproportionation of i-bu-

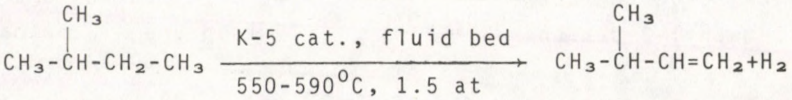
1.1 Isoprene recovery from pyrolysis C_5-fraction by extractive distillation (BASF, JSR, Shell, etc. process)

1.2 Recovery and dehydrogenation of isoamylene (Dow Process)

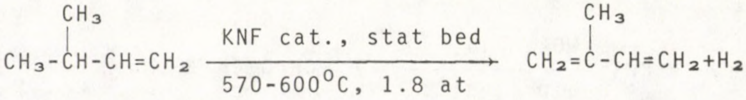


$$CH_3-\overset{CH_3}{\overset{|}{C}}-CH=CH_2 \xrightarrow[550-600^{o}C,\ 1.5-1.8\ \text{at}]{\text{Dow B-catalyst}} CH_2=C-CH=CH_2+H_2$$

1.3 From isopentane by a two-stage dehydrogenation (Soviet process)

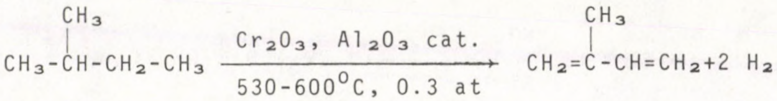


$$CH_3-\overset{CH_3}{\overset{|}{C}}H-CH_2-CH_3 \xrightarrow[550-590^{o}C,\ 1.5\ \text{at}]{\text{K-5 cat., fluid bed}} CH_3-\overset{CH_3}{\overset{|}{C}}H-CH=CH_2+H_2$$



$$CH_3-\overset{CH_3}{\overset{|}{C}}H-CH=CH_2 \xrightarrow[570-600^{o}C,\ 1.8\ \text{at}]{\text{KNF cat., stat bed}} CH_2=\overset{CH_3}{\overset{|}{C}}-CH=CH_2+H_2$$

1.4 From isopentane by a single-stage dehydrogenation (Houdry process)



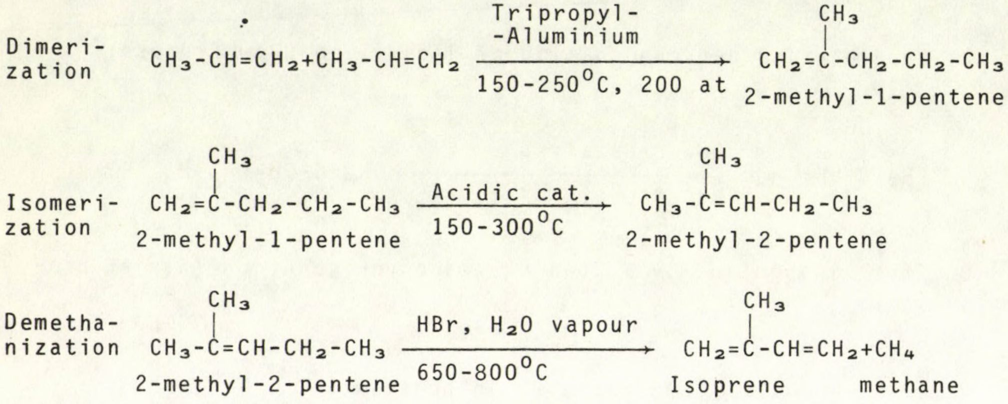
$$CH_3-\overset{CH_3}{\overset{|}{C}}H-CH_2-CH_3 \xrightarrow[530-600^{o}C,\ 0.3\ \text{at}]{Cr_2O_3,\ Al_2O_3\ \text{cat.}} CH_2=\overset{CH_3}{\overset{|}{C}}-CH=CH_2+2\ H_2$$

Fig.2. 1. Isoprene production from ordinary C_5-fraction

tene and propylene or i-butene and n-butene-2 and by applying the Dow B catalyst, the product is converted to isoprene (similar to the case of isoamylene in the Acro-Stratford-Shell process).

The third group consists of those C_5 chain syntheses which are based partly on the application of hydrocarbons and partly on the use of intermediary compounds containing oxygen (Figure 4).

2.1 Isoprene production from propylene (Goodyear SD process)

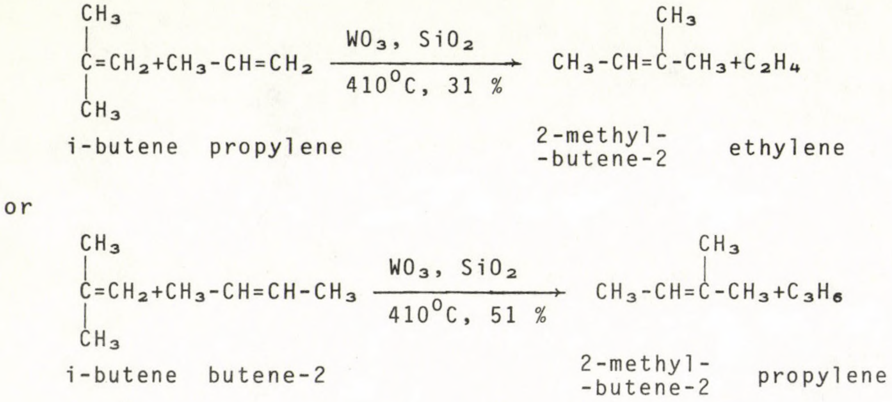


Dimerization $$CH_3-CH=CH_2+CH_3-CH=CH_2 \xrightarrow[150-250^{\circ}C,\ 200\ at]{Tripropyl-Aluminium} \overset{\displaystyle CH_3}{\overset{|}{CH_2=C}}-CH_2-CH_2-CH_3$$ 2-methyl-1-pentene

Isomerization $$\overset{\displaystyle CH_3}{\overset{|}{CH_2=C}}-CH_2-CH_2-CH_3 \xrightarrow[150-300^{\circ}C]{Acidic\ cat.} \overset{\displaystyle CH_3}{\overset{|}{CH_3-C}}=CH-CH_2-CH_3$$ 2-methyl-1-pentene → 2-methyl-2-pentene

Demethanization $$\overset{\displaystyle CH_3}{\overset{|}{CH_3-C}}=CH-CH_2-CH_3 \xrightarrow[650-800^{\circ}C]{HBr,\ H_2O\ vapour} \overset{\displaystyle CH_3}{\overset{|}{CH_2=C}}-CH=CH_2+CH_4$$ 2-methyl-2-pentene → Isoprene methane

2.2 Isoamylene production by disproportionation (Phillips process)



$$\underset{\displaystyle CH_3}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{C}}}}=CH_2+CH_3-CH=CH_2 \xrightarrow[410^{\circ}C,\ 31\ \%]{WO_3,\ SiO_2} \overset{\displaystyle CH_3}{\overset{|}{CH_3-CH=C}}-CH_3+C_2H_4$$

i-butene propylene 2-methyl-butene-2 ethylene

or

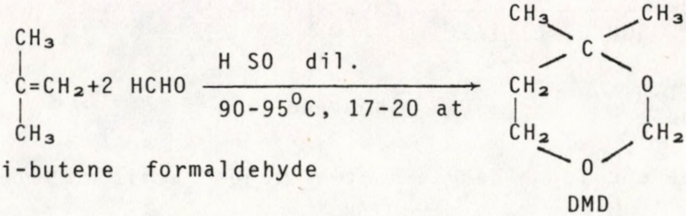
$$\underset{\displaystyle CH_3}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{C}}}}=CH_2+CH_3-CH=CH-CH_3 \xrightarrow[410^{\circ}C,\ 51\ \%]{WO_3,\ SiO_2} \overset{\displaystyle CH_3}{\overset{|}{CH_3-CH=C}}-CH_3+C_3H_6$$

i-butene butene-2 2-methyl-butene-2 propylene

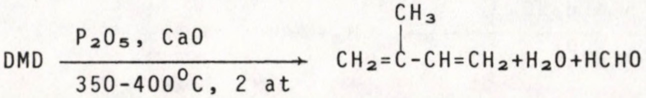
Fig.3. 2. Isoprene production by the synthesis of C_5 chain from hydrocarbons

Many of these processes are based on the use of i-butene and formaldehyde, and on the Prins reaction. The dimethyl dioxane obtained is converted to isoprene, even if the process is single-stage and the dimethyl dioxane is treated as on intermediary pro-

3.1 From i-butene and formaldehyde (through DMD) (Soviet, IFP, Bayer process)


i-butene formaldehyde

DMD



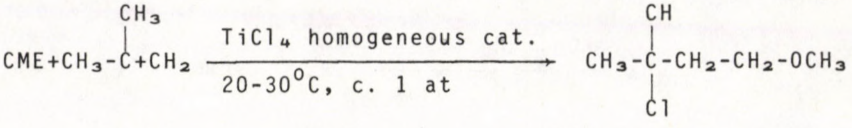
$$\mathrm{DMD} \xrightarrow[350\text{-}400^{\circ}C,\ 2\ at]{P_2O_5,\ CaO} CH_2{=}\overset{CH_3}{\overset{|}{C}}{-}CH{=}CH_2 + H_2O + HCHO$$

3.2 From i-butene and formaldehyde (through chloromethyl butyl methyl ether) (Marathon Oil process)

Chloromethylmethylether formation:

$$HCHO + CH_3OH + HCl \xrightarrow[20\text{-}30^{\circ}C,\ c.\ 1\ at]{} ClCH_2OCH_3 + H_2O$$

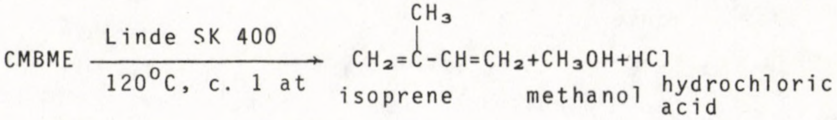
formal- dehyde metha- nol hydrochloric acid Chloromethylmethylether (CME)



$$\mathrm{CME} + CH_3{-}\overset{CH_3}{\overset{|}{C}}{+}CH_2 \xrightarrow[20\text{-}30^{\circ}C,\ c.\ 1\ at]{TiCl_4\ \text{homogeneous cat.}} CH_3{-}\underset{Cl}{\underset{|}{\overset{CH}{\overset{|}{C}}}}{-}CH_2{-}CH_2{-}OCH_3$$

i-butene

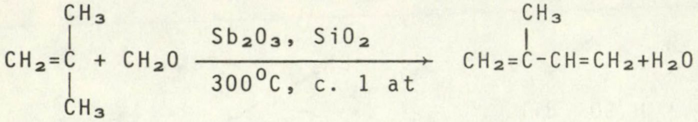
3-chloro-3-methylbutyl-methylether (CMBME)



$$\mathrm{CMBME} \xrightarrow[120^{\circ}C,\ c.\ 1\ at]{\text{Linde SK 400}} CH_2{=}\overset{CH_3}{\overset{|}{C}}{-}CH{=}CH_2 + CH_3OH + HCl$$

isoprene methanol hydrochloric acid

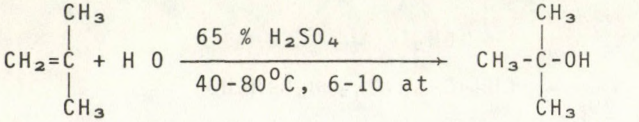
3.3 From i-butene and formaldehyde in one-stage (Takeda process)



$$CH_2{=}\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}} + CH_2O \xrightarrow[300^{o}C,\ c.\ 1\ at]{Sb_2O_3,\ SiO_2} CH_2{=}\overset{\displaystyle CH_3}{C}{-}CH{=}CH_2{+}H_2O$$

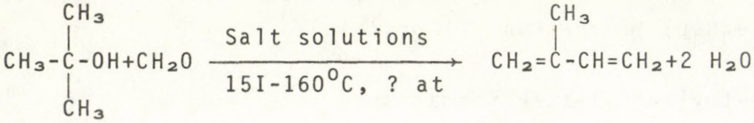
i-butene formaldehyde isoprene

3.4 From i-butene and formaldehyde in two-stages (Sumitomo Process)



$$CH_2{=}\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}} + H\ O \xrightarrow[40\text{-}80^{o}C,\ 6\text{-}10\ at]{65\ \%\ H_2SO_4} CH_3{-}\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}{-}OH$$

i-butene tert.-butanol

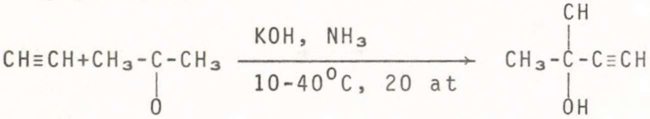


$$CH_3{-}\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}{-}OH{+}CH_2O \xrightarrow[15I\text{-}160^{o}C,\ ?\ at]{Salt\ solutions} CH_2{=}\overset{\displaystyle CH_3}{C}{-}CH{=}CH_2{+}2\ H_2O$$

tert.-butanol formaldehyde isoprene

3.5 From acetylene and acetone (SNAM-Progetti process)

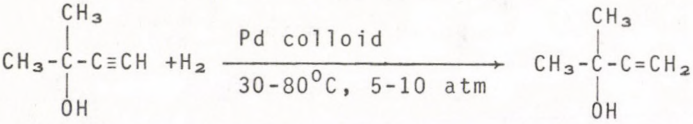
Ethynylation:



$$CH{\equiv}CH{+}CH_3{-}\underset{\displaystyle O}{C}{-}CH_3 \xrightarrow[10\text{-}40^{o}C,\ 20\ at]{KOH,\ NH_3} CH_3{-}\overset{\displaystyle CH}{\underset{\displaystyle OH}{C}}{-}C{\equiv}CH$$

acethylene aceton 3-methylbutyn-1-ol-3 (MBI)

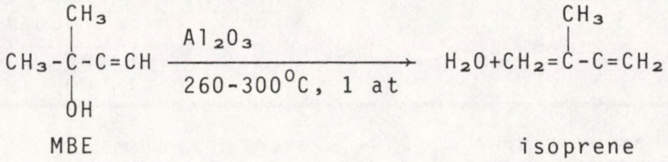
Selective hydrogenation:



$$CH_3{-}\overset{\displaystyle CH_3}{\underset{\displaystyle OH}{C}}{-}C{\equiv}CH\ {+}H_2 \xrightarrow[30\text{-}80^{o}C,\ 5\text{-}10\ atm]{Pd\ colloid} CH_3{-}\overset{\displaystyle CH_3}{\underset{\displaystyle OH}{C}}{-}C{=}CH_2$$

(MBI) 3-methylbutene-1-ol-3 (MBE)

Dehydration:



$$CH_3\text{-}\underset{OH}{\overset{CH_3}{C}}\text{-}C{\equiv}CH \xrightarrow[260\text{-}300^{0}C,\ 1\ at]{Al_2O_3} H_2O + CH_2{=}\overset{CH_3}{C}\text{-}C{=}CH_2$$

Fig.4. 3. Isoprene production by the synthesis of C_5 chain from hydrocarbons and intermediaries containing oxygen

duct. This differs from the Marathon Oil Company process which is also based on i-butene and formaldehyde as the starting material.

The SNAM-Progetti process is totally different and is based on the reaction of acetylene and acetone in which acetylene alcohol, 3-methyl butyne-=-ol-3 is produced.

Table 2. gives a review of the planned and realized isoprene capacities.

Table 3. shows a summary of the requirements that isoprene monomers should fulfil. The general rule is that stereospecific polimers of high cis-isomer can be produced only from highly pure monomers.

Table 4. gives a summary of the basic material consumption data for the process and amounts of the byproducts. It is clear from the data that 1.5-2.7 tons of raw material are needed for the preparation of 1 ton of isoprene.(In the Acro-Shell process 7.5-10 tons of cracked gasoline cuts are needed to produce 1.5 tons of isoamylene). The processes are not selective and so some byproducts are obtained. By marketing these byproducts, the process can be made more economical.

In addition to the low utilization of materials some of these process require high energy costs, as is shown by the energy consumption data in Table 5. Investment costs are also considerable (Table 6). These data should be treated with care as they are not very trustworthy.

Table 2. The data of known isoprene plants

Company	Location	Process	Output Present	 Planned
			1,000 t/year	
Enjay	Baton Rouge USA	FCC-C_5 extr.	6.0	...
Goodyear	USA, Beaumont	Goodyear SD	50.0	...
		Arco-ACN	25.0	...
Shell	USA, Marietta, Torrance	Arco-Shell-Dow	64.0	...
Goodrich-Gulf	USA, Port Neches	Arco-Shell-Dow	55.0	...
Shell	Holland Pernis	Arco-Shell-Dow	70.0	+30.0
ANIC	Italy Ravenny	SNAM-Progetti	30.0	...
	SU, various sites	i-butene + formaldehyde min.	100.0	...
		i-pentane deh. min.	120.0	...
Erdölchemie/ /BASF	FRG, Dormagen	NMP extr.dist.	...	+80.0
Japan Geon	Japan	DMF extr.dist.	...	+30.0
Japan Synthetic Rubber	Japan	DMF (ACN?) extr.dist.	...	+30.0
Asahi Chem.	Japan	extr.dist.	...	+30.0
Kurashiki Rayon	Japan	i-butene + formaldehyde	...	+30.0
Kombinat Georghiu Dej	RSR	Soviet	...	+60.0
			520.0	+290.0

Table 3. The purity requirements for isoprene to be applied as the monomer of synthetic caoutchouc in the stereoregular polymerization process

Process		x	BASF-EC	IFP	Sumitomo	SNAM Progetti
Isoprene	min.	97.0 wt%	99.0 wt%	99.4 wt%	99.5 wt%	98.5 wt%
Paraffin hydrocarbons	max.	...	...	...	...	100 ppm
Olefins	max.	3.8 wt%	0.5 wt%	0.6 wt%	0.15 wt%	1.5 wt%
Acetylene (+allenes)	max.	100 ppm	100 ppm	100 ppm	...	50 ppm
Cyclopentadiene	max.	1 ppm	1 ppm	50 ppm	0	...
Dimer-isoprene	max.	0.1 wt%	...	...	...	100 ppm
Piperylene	max.	80 ppm	...	...	0	...
Cyclopentene	max.	...	...	100 ppm	0	0
Organic compds.containing O, S (in carbonyls, H_2S)	max.	55 ppm	55 ppm	0	...	200 ppm
Peroxides	max.	5 ppm	...	...	...	0
Acetonitrile	max.	8 ppm	...	...	...	...

[x] September 1971 issue of Chemical Eng., considered typically suitable for cis-polymerization. The permissible olefin content is too high and the isoprene concentration too low.

Table 4. Basic material consumption data of some of the processes for isprene production (per 1 ton of isoprene)

Process	Material	Production/1 ton of isoprene
SNAM-Progetti	Acetone	0.97 ton
	Acetylene	0.43 ton
	Hydrogen	400 Nm^3
	Ammonia	5 kg
Goodyear SD	Propylene	2.67 ton
	Byproduct	1.30 ton
IFP	i-Butene	1.04 ton
	Methanol	0.99 ton
	Byproducts	0.51 ton
Bayer	i-Butene	0.95 ton
	Methanol	0.85 ton
	Byproducts	0.25 ton
Soviet	i-Butene	1.28 ton
	Methanol	1.10 ton
	Byproducts	0.30 ton
Arco-Shell-Dow	i-Amylene	1.50 ton
Houdry	i-Pentane	2.20 ton
	Byproducts (piperylene)	0.40 ton
Phillips-Dow	i-Butene	1.13 ton
	n-Butene-2	0.57 ton
	Byproducts (propylene)	0.35 ton
Extractiv dist. (BASF, JSR, etc.)	C_5-fraction (pyrolysis)	5.00 ton
	Byproducts	
	CPD	1.00 ton
	C_5-fraction	3.00 ton

Table 5. Basic material consumption data of some of the processes for isoprene production (services per 1 ton of isoprene)

Process	Vapour t	Electr. energy kWh	Cooling water m³	Heating material G-cal
SNAM-Progetti	5	600	350	0.34
Goodyear SD	27	300	1,000	-
IFP	10	320	140	7
Bayer	7.8	440	220	1.2
Arco-Shell-Dow	24.5	600	1,000	7.5
Houdry	14.8	2,600	600	4
Soviet (Prins reaction)	22	630	400	3
BASF-Erdölchemie (NMP)	9.5	190	480	-
SNAM-Progetti (extr.dest.)	12.7	87	960	-
Japan Geon (DMF)	10	150	500	-
Phillips-Dow	22	250	550	6.8

Utilizing the earlier mentioned data, and more or less arbitrary unit prices and expenses, the cost data shown in Table 7. were calculated. The total cost column consisted of the material and capital expenses only, and did not represent the total production costs.

The column of "sum total of costs" convincingly shows that isoprene production is a considerably expensive operation. The average cost of the first two processes is 250 + 20 $t, in other words, the cost data fall within a range of ±10 %. The total costs of isoprene production from pyrolysis C_5 fractions are relatively low. This would amount to a tolerable 160 $t as basic costs.

Table 6. Investment expenditures on isoprene production (1971/1972 data)

Process	Output ton/yr	Investmen costs M$	Specific investment costs ($/ton/yr)	Note
Extractive distillation NMP (BASF-EC)	30,000	4.7±20 %	155±30	
SNAM-Progetti	60,000	21	350	(1)
Goodyear SD	60,000	24	400	(1)
IFP-Bayer	60,000	30	500	(1)
Arco-Shell-Dow	60,000	16.7	280	
Houdry	60,000	19.2	320	
Acetonitrile extractive distillation	20,000	3.45	172.5	
Soviet i-butene + formaldehyde	60,000	13.43	270	(2)
Japan Geon - DMF	45,000	6,4	142	
Takeda single-stage	60,000	10.7	178	
Phillips disproportionation + Arco + Dow	100,000	16.2	162	

(1) Th. Reis estimate

(2) Power Gas Corp. estimate

Dr. Duck would welcome isoprene from the JSR that could be so cheap. According to him isoprene can compete with natural caoutchouc, only if its price or cost is exactly 200 $t.

Despite the above mentioned economically favourable conditions, the recevery of the isoprene content of pyrolysis C_5 fractions has not gained wide application. The main reason is that both the quantity of the C_5 fraction and hence its isoprene content are insignificant, as can be seen from the composition data of Table 8.

Table 7. Calculated costs of isoprene production ($/ton)

Process	Output, 1,000 ton/yr	Overall material cost	Byproduct credit (-)	Net material cost	Energy	Capital expenditure	Total costs
SNAM-Progetti	30	180	0	180	20	70	270
Goodyear SD	60	150	-65	85	65	80	230
IFP	60	180	-50	130	40	100	270
Bayer	60	155	-25	130	25	100	255
Soviet (Prins)	60	206	-60	146	60	54	260
Arco-Shell-Dow	60	120	-	120	80	56	256
Houdry	60	156	-40	116	70	74	260
Phillips-Dow	100	130	-22	108	66	32	206
Extractive distillation, C_5-fraction	20	400	-300	100	28	32	160

Table 8. The detailed composition of the pyrolysis C_5-fraction according to BASF and Erdölchemie

Butane-2 (cis+trans)	1.6 wt%	
Butadiene-1,3	0.3 wt%	
Butadiene-1,2	0.6 wt%	
Butyn-2	0.4 wt%	
Total C_4 hydrocarbons		2.9 wt%
Cyclopentane	1.0 wt%	
n-Pentane	16.57 wt%	
i-Pentane	13.0 wt%	
Penten-1	3.5 wt%	
Pentene-2 (cis+trans)	3.5 wt%	
2-(and 3-)-methylbutene-1	7.0 wt%	
2-methylbutene-2	3.3 wt%	
Cyclopentene	2.5 wt%	
Isoprene	18.0 wt%	
Piperylene (cis)	4.0 wt%	
Piperylene (trans)	6.5 wt%	
Pentadiene-1,4	1.8 wt%	
Cyclopentadiene Dicyclopentadiene }	16.0 wt%	
Isopropylacetylene	0.035 wt%	
Isopropenylacetylene	0.035 wt%	
Pentyn-1	0.03 wt%	
Pentyn-2	0.03 wt%	
Total C_5 hydrocarbons		96.8 wt%
C_{6+} hydrocarbons	0.3 wt%	0.3 wt%
	100.0 wt%	100.0 wt%

Table 9. The group composition of pyrolysis C_5-fraction according to BASF and Erdölchemie

C_4 monoolefin	1.6 wt%
C_4 diolefin	0.9 wt%
C_4 acetylene	0.4 wt%
C_5 paraffins	29.57 wt%
C_5 monoolefins	17.3 wt%
Isoprene	18.0 wt%
Other straight-chained C_5 diolefins	12.3 wt%
C_5 cycloparaffin	1.0 wt%
C_5 cycloolefin	2.5 wt%
C_5 cyclodiolefin (DCP too)	16.0 wt%
C_5 acetylenes	0.13 wt%
C_{6+}	0.3 wt%
	100.0 wt%

For each ton of ethylene, 300-400 kg of C_4 fraction are obtained (of which the amount of butadiene is 120-150 kg) from gasoline pyrolysis, whilst the amount of C_5 fraction is much smaller (100-200 kg) and of this, the amount of isoprene is 20-60 kg per 1 ton of ethylene. Thus, fairly high ethylene outputs are necessary for the required amount of fraction to accumulate. For example, the planned Bayer plant with an output of 80,000 tons a year would require, for the necessary C_5 fraction, ethylene production of a capacity of 2 million tons a year.

The present disorder in world prices makes it difficult to visualize the future of cis-polyisoprene caoutchouc.

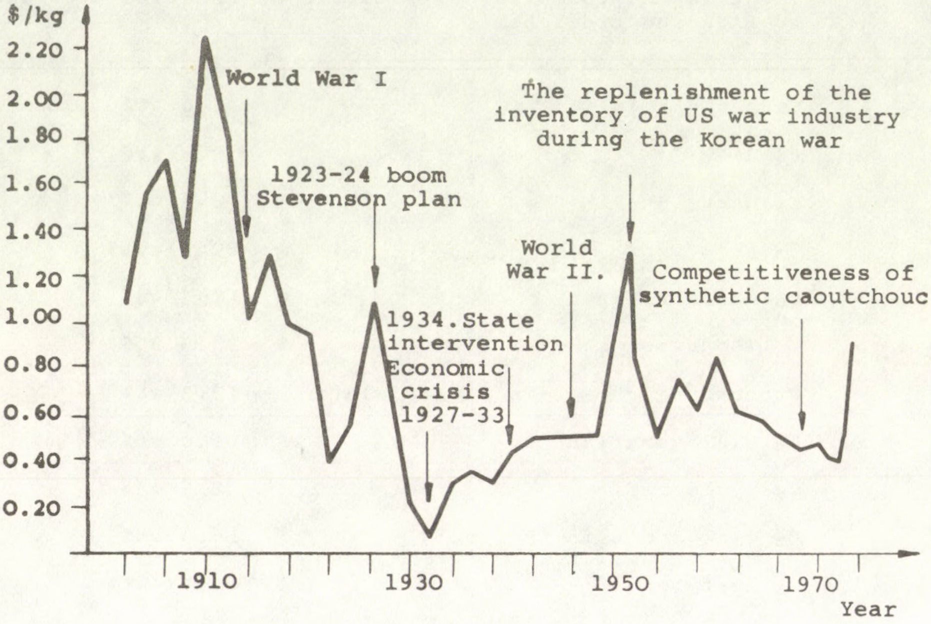


Fig.5. The trend of caoutchouc prices since 1900

If prices were to remain stable at a high level, then cis-isopolyisoprene caoutchouc would be able to compete with natural caoutchouc. High prices would encourage the investiment of caoutchouc plantation and the establishment of new plants for the manufacture of synthetic caoutchouc. Since the latter solution is more feasible, considering that plantations become arable only after 7 years, as opposed to the transit period of 2.5-4 years for industrial establishments. This would result in the installation of more isoprene monomer and polimerization plants in the future.

For the processes to be more widely accepted, it would be advisable to improve the applicability of the byproducts. To achieve this, it is necessary to carry out technological and utilization studies on all those processes accompanied by large quantities of byproducts.

In this respect, some of the processes differ basically. In the Phillips Triolefin process, for example, the byproduct is ethylene or propylene, whose utilization is no problem.

The problem is not so easy in the case of isopentane dehydrogenation (for example, the Soviet two-stage or Houdry single-stage process) where the byproducts are n-pentadienes and piperylenes. Their quantity ranges between 0.3-0.4 t/t isoprene, which is considerable. Research work has been carried out on the preparation of special caoutchouc based on piperylenes and the production of latex of excellent properties, but these projects would not be able to use up the total amount of the available piperylene.

A similar problem exists in the case of cyclopentadiene obtained from pyrolysis C_5 fraction. Although it is applied in the chemical industry (in the production of plant protective, and in thermonomer ethylene-propylene caoutchouc, etc.) its market is fairly limited. Its quantity would nearly equal that of isoprene and its marketing at a good price would hardly be feasible. With the Bayer process, a considerable amount of a new elastomer - the trans-polypentenamer - is formed. The monomer of this special caoutchouc is cyclopentene and can be prepared by the selective hydrogenation of cyclopentadiene. The only problem connected with the elastomer is that its properties are so good that it may be able to compete with the cis-polyisoprene itself.

It is worthwhile discussing the problems connected with the byproducts of the syntheses based on i-butene and formaldehyde (through dimethyl dioxane). In this respect, research work was carried out at the MÁFKI in the past decades.

In the processes based on the Prins reaction, 0.25-0.5 ton of byproducts per 1 ton of isoprene are obtained. French technologists separated them into two fractions (Residol I and II). The byproducts of the Soviet process are obtained in various fractions which may, depending on where they are obtained, be green oils, light and heavy residues and bottom products.

A part of these fractions can be converted back to the starting materials (formaldehyde, methanol, and isobutene) and by submitting them to appropriate treatment, the consumption of basic material can be reduced. A heavy distillate is also obtained which can be converted to isoprene, thereby raising the yield of the latter. These measures are included in the Soviet projects. According to the Giprocaoutchouc data, only 0.3 ton of byproduct should be expected and the plant results are even more favourable, for by recycling some of the byproduct fluxes, the equilibrium can be shifted so that more of the desired product (e.g. DMD) is formed, thereby increasing the yield.

Despite the above facts, the utilization of the byproducts - consisting of such compounds as polyalcohols (diols, triols), ethers, dioxanes and dioxane alcohols, tetrahydropyrane and considerable amounts of unsaturated and saturated hydrocarbons - proved to be a serious problem. Indeed, some of the distillates and residues have not yet been analyzed in detail and until then there is no sense in starting application studies on them.

The staff of the Analytical Department at the MÁFKI undertook the complete analysis of Soviet plant samples and so far appreciable results have been obtained. The details deserve a report of their own by the research-workers and are therefore outside the scope of this article. By way of example, it can be mentioned that 10, 47, 59 and 98 components were identified in the fractions of methanol-methylel, the bottom products of dioxane synthesis and isoprene purification and green oil, respectively, examined at MÁFKI and some of these components were quantitatively analyzed.

Unfortunately the analysis was discontinued, as all the plans to produce caoutchouc domestically were cancelled, but the experience gained and the methods developed will prove useful in the implementation of the complex programme designed by the C.M.E.A. countries, in which a large cis-polyisoprene caoutchouc plant will be built in Bucharest. This programme is of direct interest to Hungary.

Apart from the recovery and marketing of the main products, the detailed analysis of the byproducts is also necessary in order to improve the synthesis, the conversion, the product recovery and the formation of byproducts that accompanies some of the isoprene purification operations. In this way, the required amount of basic material may be reduced and the entire production process becomes more economical.

The C.M.E.A. research contract programme makes it possible for the MÁFKI to take part in the project.

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РЕЗЮМЕ

В середине пятидесятых гг. модернизированными каталитическими системами Циглера-Натты выработаны несколько методов получения 1,4-цис-полиизопрена. Вопреки тому, что полученные таким методом эластомеры соответствуют природному каучуку, развитие производственной мощности тормозится недостаточным до сих пор снабжением мономерами. Проблема состоит в том, что себестоимость мономера высока, а цена полимерного природного каучука сравнительно низка, поэтому возникалось противоречие между себестоимостью и сниженной ценой мономера.

Это обстоятельство изменится вдруг в случае повышения цены природного каучука, потому что для производства изопрена имеется много способов и из этих многие уже внедрены.

Разработанные или уже внедренные процессы разделяются на три группы, в частности, процессы -

- использующие C_5-углеводороды природного происхождения,
- использующие углеводороды с 5-членной цепью углерода соответствующей конфигурации, полученные синтезом других углеводородов,
- использующие отчасти углеводороды, отчасты кислородо-содержащие интермедиеры.

Для производства изопрена вообще характерно, что его потребность в первичных затратах сравнительно высока. Суммарные затраты сравнительно не высокие при производстве изопрена из C_5-франции пиробензина, но серьезной проблемой здесь является достаточно высокая потребность в объеме этилена для обеспечения соответствующего количества C_5-франции.

Важнейшие условия намеренного роста производства цис-полиизопрена сводятся к следующему:

- стабилизация цен каучуков на достаточно высоком уровне,
- решение вопроса использования побочных продуктов процессов.

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ESTIMATION OF THE PHYSICO-CHEMICAL DATA OF HYDROCARBON REACTIONS BY RADIOCHEMICAL METHODS

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When alkane hydrocarbons are irradiated their chemical bonds dissociate in the following increasing order: primary < secondary < tertiary < quarternary. The radiolysis of cycloalkanes is enhanced by their strain energy: Rings of 3-4 carbon atoms break up very easily, partly by a multiple C-C bond dissociation, whilst for C_7-C_{10} cycloalkanes hydrogenation is more frequent. The radiolysis of alkenes is similar to that of alkanes, but the bond dissociation is influenced by the position of the π-bond. The $G(H_2)$ value of aliphatic alkenes can be estimated from the H-increments of $G(H_2)$.

For the past ten years, experiments were carried out at the Isotope Institute to establish the relationship between the chemical structure and the bond dissociation (by radiochemical methods) of hydrocarbons. The authors studied the radiolysis of straight-chained and cyclic, as well as saturated and unsaturated hydrocarbons, and hydrocarbon systems of various carbon numbers. The evaluation was performed by the gas chromatographic analysis of products liberated at 25-35 °C in the liquid phase as a result of the γ-radiation of radioactive isotope ^{60}Co possessing an energy and dose of 1.17-1.33 MeV and 3-8 Mrad respectively [1].The yields are represented by the G-values, i.e. the number of molecules dissociated, or molecules, atoms, radicals and ions liberated by the absorption of radiation energy of 100 eV.

In the following discussion, some examples are given of the research results which shoved a correlation between the energetic states of the hydrocarbon molecules and radiolysis.

The Effect of Branching on the Radiolysis of Aliphatic Hydrocarbons

In the past few years, many articles have been published on dehydrogenation effected by radiation, i.e. the relationships between the C-H bond dissociation processes and the molecular structure [2]. It was established that the radiochemical dissociation of C-H bonds is influenced by the position of the carbon atom (i.e. primary and secondary, etc.) and the bond energy [3, 4, 5] (Figure 1.)

Figure 2. shows the radiochemical yields of the important hydrocarbon products (grouped according to the number of carbon atoms) obtained by the irradiation of hexane isomers and illustrating, in general, the C-C bond dissociation of the molecule [6]. It can be seen that the majority are fragment products, that is to say, C_1-C_5 hydrocarbons of a molecular weight smaller than that of hexane, but the yield of C_7-C_{12} fraction was also significant.

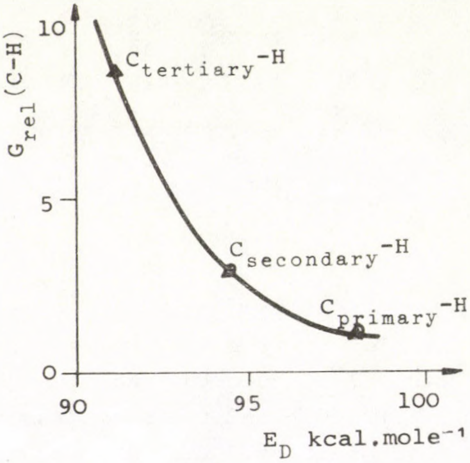


Fig.1. The dependence of radiolytic dehydrogenation of aliphatic hydrocarbons on their bond dissociation energies. Δ [4] o [3, 5]

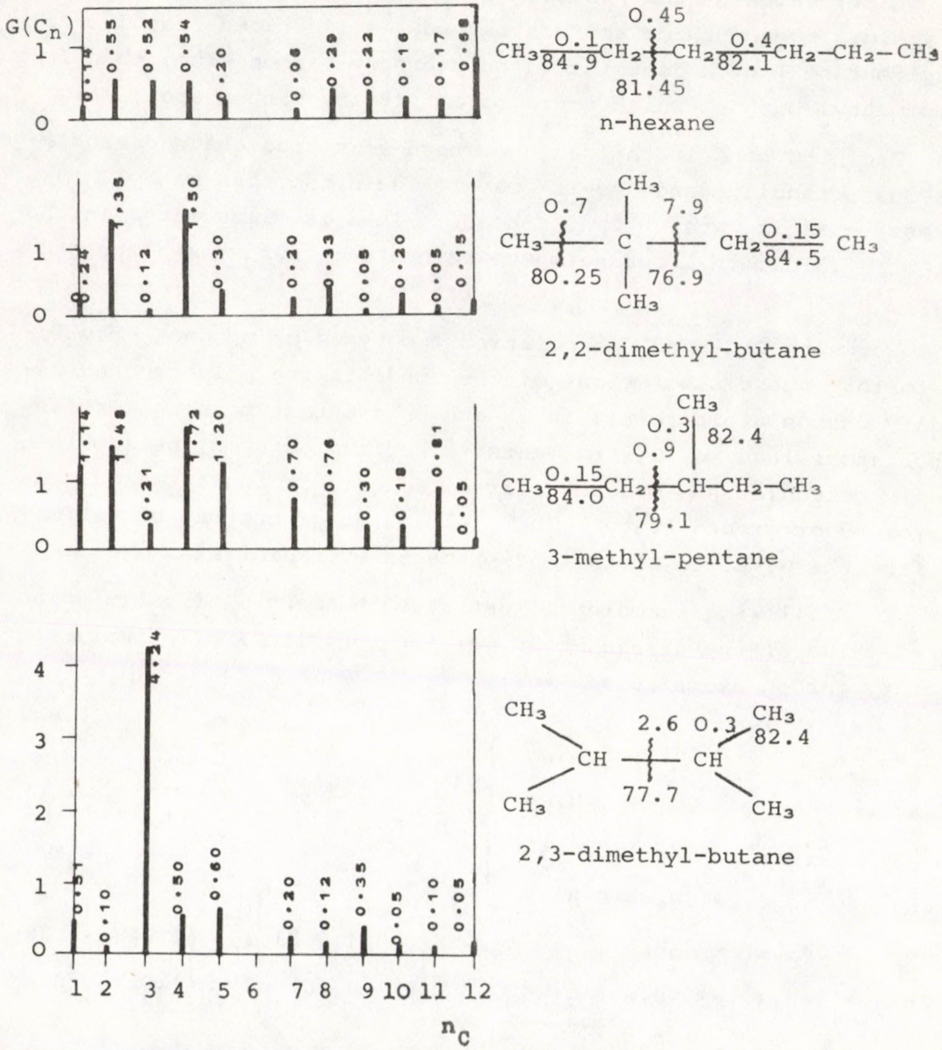


Fig.2. The yield of fractions formed radiolytically from hexane isomers. n_C - the carbon number of the product; $G(C_n)$ yield of the product

The yields of methane increased in the following order of starting materials: n-hexane < 3-methyl pentane < 2,3-dimethyl butane < 2,2-dimethyl butane, hence it was concluded that apart from the definite correlation between the number of methyl groups and the $G(CH_4)$ values, the position of the methyl group also affects the yield. Indeed, twice as much methane is liberated from 2,2-dimethyl butane (which contains a quarternary carbon atom) than from 2,3-dimethyl butane (which contains a tertiary carbon atom).

The C-C bond in the neighbourhood of a side chain dissociates most readily and so it may be said that the methyl group weakens - as it were - the β-bonds. This is illustrated in the case of 2,3-dimethyl butane where both branchings weaken the same bond.

For each C-C bond dissociation two types of products may issue forth; the dissociations of the bond linking primary and secondary carbon atoms result in C_1 and C_5 and that poining tertiary carbon atoms lead to C_3 fragments. The fragments may be simultaneously molecular end-products, free radicals or ionic radicals in an excited or ground state. The yield of fragments may be estimated from the G-values of the end-products of radiolysis.

The following example illustrated the method of calculating the G-value of the dissociation of the bond linking primary and tertiary carbon atoms [6]:

$$\left.\begin{array}{lcl}
C_6H_4{}^+ & \rightarrow & CH_4 + C_5H_{10}{}^+ \\
C_6H_{14}{}^x & \rightarrow & CH_4 + C_5H_{10} \\
CH_3^\cdot + C_6H_{14} & \rightarrow & CH_4 + C_6H_{13}^\cdot \\
CH_3^\cdot + C_xH_{2x+1} & \rightarrow & CH_4 + C_xH_{2x}
\end{array}\right\} \quad G(CH_4)=0.51 \quad G_{red}(CH_4)=+0.51$$

$$CH_3^\cdot + CH_3^\cdot \rightarrow C_2H_6 \qquad G(C_2H_6)=0.03 \quad G_{red}(C_2H_6)=+0.06$$

$$CH_3^\cdot + C_7H_{13}^\cdot \rightarrow C_7H_{16} \qquad G(C_7)=0.20 \quad G_{red}(C_7)=+0.20$$

$$H^\cdot + C_3H_6 \begin{array}{l} \nearrow \text{i-}C_3H_7^\cdot \\ \searrow \text{n-}C_3H_7^\cdot \end{array}$$

$$\left.\begin{array}{lll} CH_3^{\cdot} + i\text{-}C_3H_7^{\cdot} & \rightarrow & i\text{-}C_4H_{10} \\ CH_3^{\cdot} + n\text{-}C_3H_7^{\cdot} & \rightarrow & n\text{-}C_4H_{10} \\ CH_3 + C_3H_6 & \rightarrow & C_4H_9^{\cdot} \\ C_4H_9^{\cdot} & \begin{array}{l} \xrightarrow{+H} \\ \xrightarrow[-H]{} \end{array} & \begin{array}{l} C_4H_{10} \\ C_4H_8 \end{array} \end{array}\right\} G(C_4)=0.50 \quad G_{red}(C_4)=+0.50$$

$$i\text{-}C_3H_7^{\cdot} \rightarrow CH_3^{\cdot} + C_2H_4 \quad G(C_2H_4)=0.07 \quad \underline{G_{red}(C_2H_4)=-0.07}$$

$$\Sigma G_{red} = +1.20$$

For the dissociation of prim.C and tert.C $G = \dfrac{\Sigma G_{red}}{4} = 0.30$

By preparing a balance of the C-C dissociation products, the G-values of the dissociation of each bond shown in Figure 1. were determined. The dissociation energies of C-C bonds expressed in kcal mole^{-1} are shown below the valance lines. It can be seen that a relationship between the frequencies of bond dissociation and the dissociation energies exists (Figure 3.).

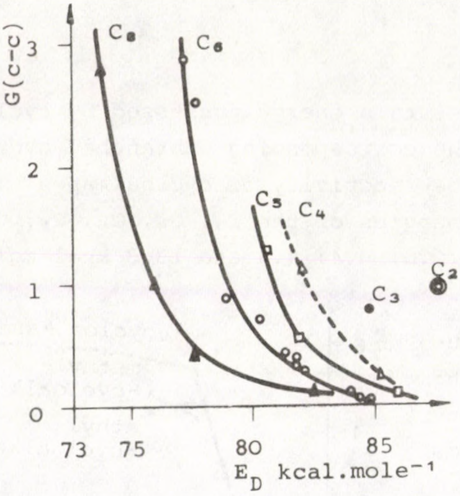


Fig.3. The dependence of the radiolytic carbon chain decomposition of alkanes on the carbon number of the fractions and its bond dissociation energy

The corresponding G(C-C) values are shown in Figure 2. above each bond of the hexane isomers studied by the authors, using the earlier mentioned method. The standard bond dissociation energies are shown below the bonds. The dependence of the values are represented by the curve C_6 in Figure 3. According to the data, the very slight differences observed amongst the dissociation energy values are significantly influenced by the dissociation processes of the irradiated molecules, despite the fact that the energy level of the excited, ionized (therefore activated) molecules before dissociation is very high (c. 250 kcal·mole^{-1}) compared to the dissociation energy.

The relationship was extended to the C_2-C_8 aliphatic hydrocarbons on the basis of literature data [3, 7-11]. The shifting of the bond dissociation energy vs. G-value curve as a function of carbon atoms shown in Figure 3. may be accounted for by the fact that the probability of the excess internal energy of the activated alkane molecules (consisting of many carbon atoms) localizing itself around the given C-C bond (or degree of freedom) is slight and the rate of disactivation (not accompanied by dissociation) increases as the length of the carbon chain increases.

The Effect of Ring Structure on the Radiolysis of Aliphatic Hydrocarbons

The formation energy termed strain energy possessed by cycloalkanes in excess of that of the corresponding unbranched hydrocarbons, significantly affects the reactivity of cycloalkanes. The numerical values of the strain energies of the C_3, C_4, C_5, C_6, C_7, C_8, and C_{10} are 27.6; 26.2; 6.3; 0.0; 6.4; 9.9 and 13.3 kcal·mole^{-1} respectively [12].

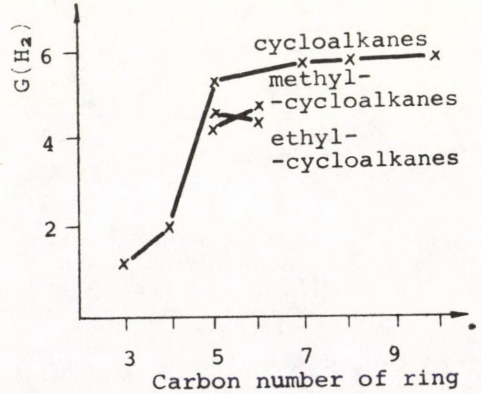


Fig.4. The components of the C-C bond dissociation energy of n-pentane and cyclopentane

From the data shown in Figure 4., it can be seen that the $G(H_2)$ values increase with the increasing number of carbon atoms within the cycloalkane rings.

The extremaly small $G(H_2)$ values [13] for cyclopropane and cyclobutane can be accounted for by the relatively low values of the bond dissociation energy (103 kcal·mole^{-1}) of the C-H bonds [13]. As a result of C-H bond dissociation, the hybridization state of the carbon atom changes from sp^3 to sp^2, its bond angle from 109.5° to 120° so that the angle strain increases,which is unfavourable to C-H bond dissociation.

The $G(H_2)$ values for cycloheptane, cyclooctane and cyclodecane are low because there exist repulsive van der Waals forces among the unfavourably situated hydrogen atoms of the cycloalkanes. The strain within the molecules is mainly caused by the said forces [14]. These repulsive forces weaken the C-H bonds and enhance the dissociation of the latter [15].

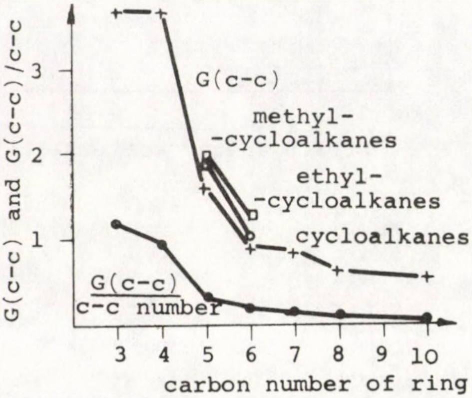


Fig.5. The dependence of radiolytic carbon-chain decomposition of cyclohexanes on the ring size

Figure 5.shows the overall G-values of unbranched,radiation-activated cycloalkanes whose C-C bonds dissociate and the G-values per C-C bond, for which it is assumed that all carbon atoms or C-C bonds are equivalent. From the diagram, it follows that the yield of the dissociated C-C bonds and the G-values of the C-C dissociations per C-C bond decrease with the increasing number of carbon atoms in the molecules, i.e. the increase in ring size [15].

The strength of the C-C bonds in cyclopropane and cyclobutane can easily be observed in thermal decomposition reactions, where relatively low activation energy is needed for their rings to break up. Their bond strength is considerably lower (by, at least, 15 $kcal \cdot mole^{-1}$) to that of straight-chained alkanes [13, 16-18]. Thus,in the course of reactions induced by radiation, they undergo a considerable ring decomposition.

By representing the G(C-C) values corresponding to each of the cycloalkane bonds as a function of the strain energy [13] (Figure 6), it is seen that the apparently obvious assumption that straining enhances ring decomposition is valid only within the C_3-C_6 range.

Despite the fact that ring decomposition accompanied by the liberation of the total strain energy is a thermodynamically favourable reaction, the rate of formation of the C-C decomposition producta in the case of non-cyclic C_7-C_{10} cycloalkanes is less than that observed for n-alkanes, indeed the yield of ring decomposition products decreases with the increase in strain energy. It can be concluded from the extraordinarly low G(C-C) values that the strength of their C-C bonds is relatively high [15, 19]. This phenomenon can be explained by the fact that in cycloalkanes with more than six carbon atoms (> C_6) the repulsive van der Waals forces among the hydrogen atoms become so significant that more energy is needed for the dissociation of the C-H bond than for that of C-C bond.

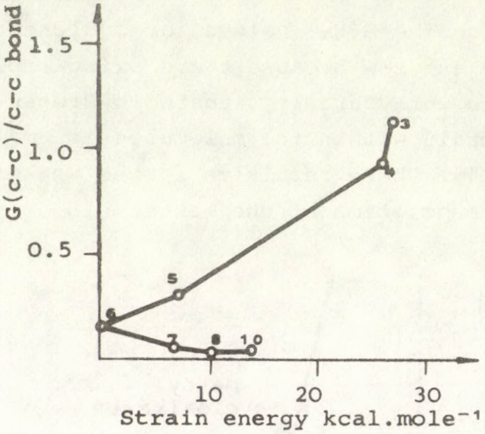
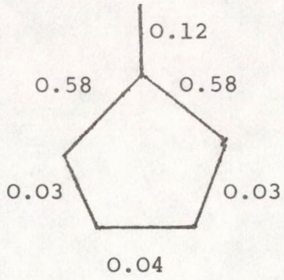
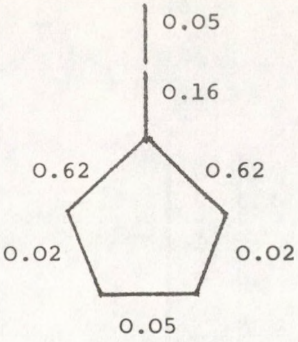


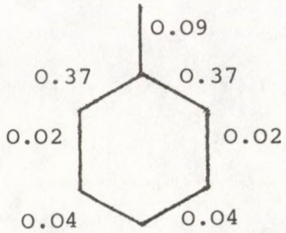
Fig.6. The dependence of carbon-chain decomposition of cycloalkanes on the carbon number of rings and ring strain energy

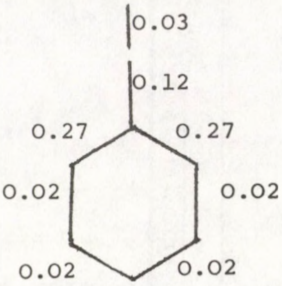
From Figure 4. it is observed that the extent of the bond dissociation of methyl, ethyl cyclopentanes and cyclohexanes is greater than that of cyclopentane and cyclohexane.This is in agreement with the fact that these molecules possess tertiary carbon atoms that are linked to C-C bonds whose strength is lower than other C-C bonds [20].

The following diagram shows the dissociation G values of some C-C bonds of alkyl cyclohexane:









The C-C bond dissociation of molecules, therefore, takes place, in most cases, at the spot where the molecule branches out and which has the least bond energy. This is similar to the radiolysis of non-cyclic alkanes.

The Effect of π-Bond on the Radiolysis of Alkenes

Table 1.summarises the yield of hydrogen liberated when some aliphatic monoalkenes are irradiated. The data indicate that the $G(H_2)$ value very much depends on the structure of the molecule. While deviation between the homologues of various carbon numbers is considerably small (Figure 7), the differences between the isomers are great. For instance, the $G(H_2)$ values of 1-hexene, 2-hexene and 3-hexene are 0.90, 1.37 and 1.64 molecule/100 eV respectively.

Table 1. The $G(H_2)$ values of aliphatic monoalkanes, the order and number of the various C-H bonds

Compound	$G(H_2)$	Allyl G-H			Non-allyl C-H	Reference
		Primary	Secondary	Tertiary		
Propylene	0.60	3	-	-	3	[21]
i-Butene	0.74	-	2	-	6	[22]
cis-2-Butene	1.02 0.96	6	-	-	2	[23]
i-Pentene	0.83	-	2	-	8	
1-Hexene	0.90	-	2	-	10	[24]
cis-, trans-2-Hexene	1.37	3	2	-	7	
trans-3-Hexene	1.64 1.61	-	4	-	8	[25]
1-Heptene	0.94	-	2	-	12	
1-Octene	0.98	-	2	-	14	
cis-, trans-2-Octene	1.42	3	2	-	11	
trans-3-Octene	1.63	-	4	-	12	
trans-4-Octene	1.61	-	4	-	12	[24]
1-Decene	1.10	-	2	-	18	
trans-5-Decene	1.70	-	4	-	16	
1-Hexadecene	1.30	-	2	-	30	[26]

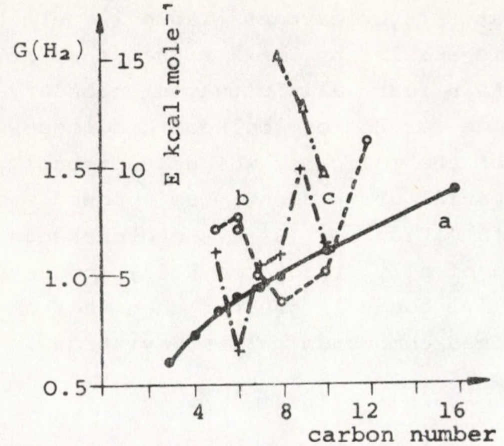


Fig.7. The dependence of radiolytic dehydrogenation of monoalkanes on the carbon number and ring strain energy of the molecule. a) 1-alkene, b) cycloalkane, c) ring strain energy, -.- cis-isomer, -..- trans--isomer

The π-bond has a basic effect [23, 27] on the radiolytic decomposition of alkenes similar to that observed for cracking [28] or photochemical decomposition [29]. The σ-bond situated in a β-position to the π-bond dissociates about ten times as easily as the bond in the α-position and this is in agreement with the energetic conditions. For instance, the dissociation of the primary allyl C-H bond requires less energy (by 16.5 kcal·mole^{-1}) than the primary vinyl σ-bond [12]. This indicates that the unpaired electron liberated during bond dissociation delocalises itself around the π-bond (allyl resonance) and consequently energy is liberated.

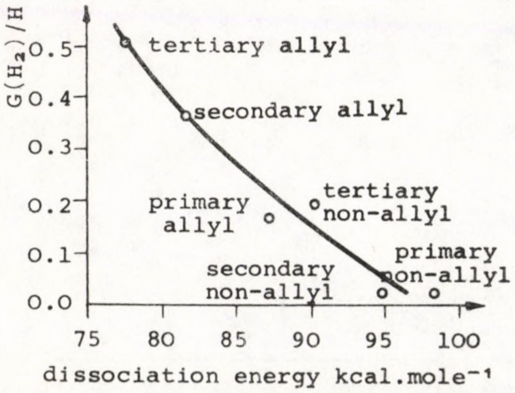


Fig.8. The dependence of radiolytic dehydrogenation of aliphatic alkenes on bond dissociation energy

Figure 8. shows the specific hydrogen yield of allyl hydrogen atoms of various orders as a function of dissociation energy. The corresponding bond energies can be estimated from the G(H_2)/H data.

$$E = \frac{3.333-G(H_2)/H}{3.612\times10^{-2}}\ \text{kcal}\cdot\text{mole}^{-1}$$

The radiolytic decomposition of cycloalkenes, like cycloalkanes, differs from that of the corresponding aliphatic hydrocarbons (Table 2); e.g. the G(H_2) value of cyclohexene is smaller by 20-25 % than that of 3-hexene, even though both contain four allylsituated secondary carbon atoms each. The G(H_2) value for the cycloalkene homologues are not a monotonous function of the molecular weight, probably because of their considerable spatial arrangement, as opposed to the aliphatic alkanes. The conformation of C_7-C_{10} cyclohexenes somewhat hinders the occurrence of allyl resonance [24], consequently the bond energy of the allyl bonds is greater than that of the corresponding straight-chained compounds. This deviation is negligible for the C_{12} ring.

Table 2. The G(H_2) values of cyclic alkenes, the number and order of the various bonds [24]

Compound	G(H_2)	Allyl C-H			Non-
		Primary	Secondary	Tertiary	allyl
Cyclopentene	1.20	-	4	-	4
Cyclohexene	1.19	-	4	-	6
Cycloheptene	0.98	-	4	-	8
cis-Cyclooctane	0.85	-	4	-	10
cis-trans-Cyclodecene	1.02	-	4	-	14
cis-trans-Cyclododecene	1.60	-	4	-	18
1-methyl-Cyclohexene	1.80	3	4	-	5
3-methyl-Cyclohexane	1.30	-	2	1	9
4-methyl-Cyclohexene	1.18	-	4	-	8
Methylene-cyclohexene	0.75	-	4	-	8

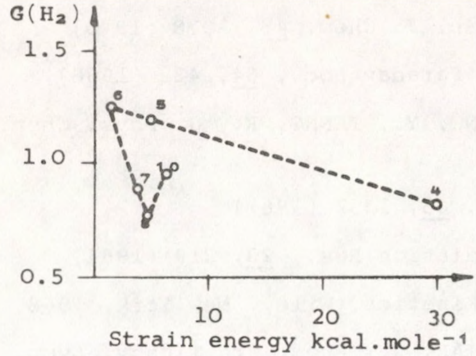


Fig.9. The dependence of radiolytic dehydrogenation of cycloalkenes on the carbon number of rings and strain energy

Comparison curves c and b in Figure 7 shows that for C_6-C_{10} rings, there exists a close negative correlation between the strain energies and the $G(H_2)$ values. This dependence is, however, represented in Figure 9 and it is clear that a tenfold increase in the strain energy results in a 20-30 % decrease of $G(H_2)$ value. This may be because the components of strain energy (angle strain, bond stretching, torsional and van der Waals repulsive forces) vary in a different manner to the ring carbon number. This problem is still being studied.

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РЕЗЮМЕ

Некоторые связи алифатических алканов в следствие воздействия облучения разлагаются в следующем нарастающем порядке вероятности разложения : первичные < вторичные < третичные < четвертичные. Радиолизису цикло-алканов способствует и энергия силы напряжения: для колец с 3-4 атомами углерода характерен мгновенный и часто многократный разрыв С-С связи, а для C_5-C_{10}-циклоалканов важнейшим процессом является дегидрогенизация. Радиолизис алкенов аналогично протекает с радиолизисом алканов, но и место связи π существенно влияет на разложение. Значение $G(H_2)$ алифатических алкенов можно оценивать зная инкременты $G(H_2)$ /H .

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ENVIRONMENTAL PROTECTION RESEARCH IN THE HUNGARIAN OIL AND GAS RESEARCH INSTITUTE

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The publication deals with the environmental protection research being carried out in the Hungarian Oil and Gas Research Institute, and with the achieved results. Concerning the smoke reduction of diesels, detailed results are given of tests, where using different additives, the soot content of the exhaust gas can be reduced by more than 50 %. Apart from this, a short account is given of the test results relating to the decrease in the lead content of high octane gasolines. In addition, the publication summarizes the test results achieved using semi-plant scale equipment and a catalyst developed for the catalytic after-burning of organic contamination found in exhaust gases that is uneconomical as far as recovery is concerned. In the review the optimum circumstances needed for the catalytic after-burning of different materials are also mentioned.

In conclusion the publication discusses the evolution made in the Institute on development and prototype use aimed at the rapid and secure determination of organic and some inorganic components that pollute the environment.

Alongside increasing industrialization on a world-wide scale, environmental pollution is continually intensifying. One of the major problems at the present time is to find the ways and means to halt further contamination. Strict official regulations induce investors, research and planning organizations to effectuate new procedures so that they meet official requirements concerning a decrease in damage to the environment.

Many problems have arisen connected with the Institute's professional sphere of activity and Hungarian circumstances. Although a decrease in environmental pollution is expected from the large increase in the use of hydrocarbons, there are, however, some fields where appropriate steps must urgently be taken.

Research has been carried out into these problems for some years now, and the introduction of research results has also come into prominence in certain fields. The problems arising in Hungary, concerning professional activity can be divided into three groups:

The first group involves those problems arising from the rapid development in the use of hydrocarbons, here the rapid increase in the number of motor vehicles, the Otto and Diesel engines and the exhaust gases originating from the motor fuel used cause a problem, especially in the towns. Decreasing pollution of this type is an important assignment.

The second research field is on gas, solid and fluid contamination, which has to be accounted for with the increase in the number of chemical industrial plants, primarily those establishments of the organic chemical industry.

The third field of research is to determine environmental pollution, follow it up and obtaining the required equipment, work out the required preventive methods.

The most important trends and the results achieved are briefly reviewed here.

In Hungary the number of petrol engines and Diesel vehicles is rapidly increasing, and this trend is similar to that in other countries with a well developed industry. The increasing use of Diesel vehicle motors results in intensive pollution of the environment throughout the world, mainly by soot and cancer causing materials, which create health and transport problems [1].

It is very complex task to solve this problem and investigations were carried out in the Institute using these fuels,together with research work on the concerned development tendencies. In the tests various foreign and Hungarian smoke decreasing additives were tried out, and their effect was checked.

The Institute collaborated in this work with the Institute of the Automotive Industry and the Hungarian National Oil and Gas Trust. During laboratory bench tests the smoke reduction obtainable was ascertained, alongside the additionally occurring effects when using certain additives

As a result of the large scale tests it was found that first of all additives of large barium content and of high basicity proved to be effective, and regarding economic use, such materials can be taken into consideration.

On the basis of the test results it was ascertained that the quantity of the high boiling-point fractions in gas oil, that is the temperature belonging to the 96 w% distillation point had a significant influence on the soot content of the exhaust gas and the efficacy of the smoke reduction.

This correlation is shown on Figure 1, where the amount of soot is shown in the function of the additive concentration and the boiling point limit the fuel used.

During the tests it was found that the soot content of the exhaust gas is also affected by the sulphur content of the diesel oil. But the sulphur content not only had an effect on the soot content, but also influenced the efficacy of the additives applied. The test results are indicated on Figure 2, which shows that when using 0.25 w% additive, the soot exhaustion with the 0.45--0.5 w% sulphur containing gas oil is 50 % lower than originally.

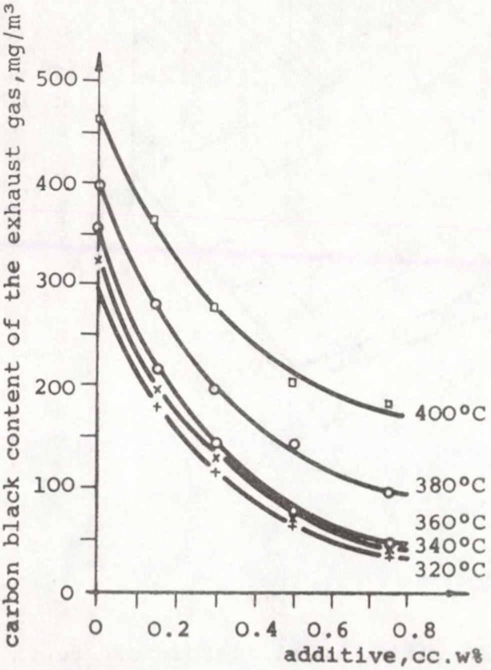

Fig.1

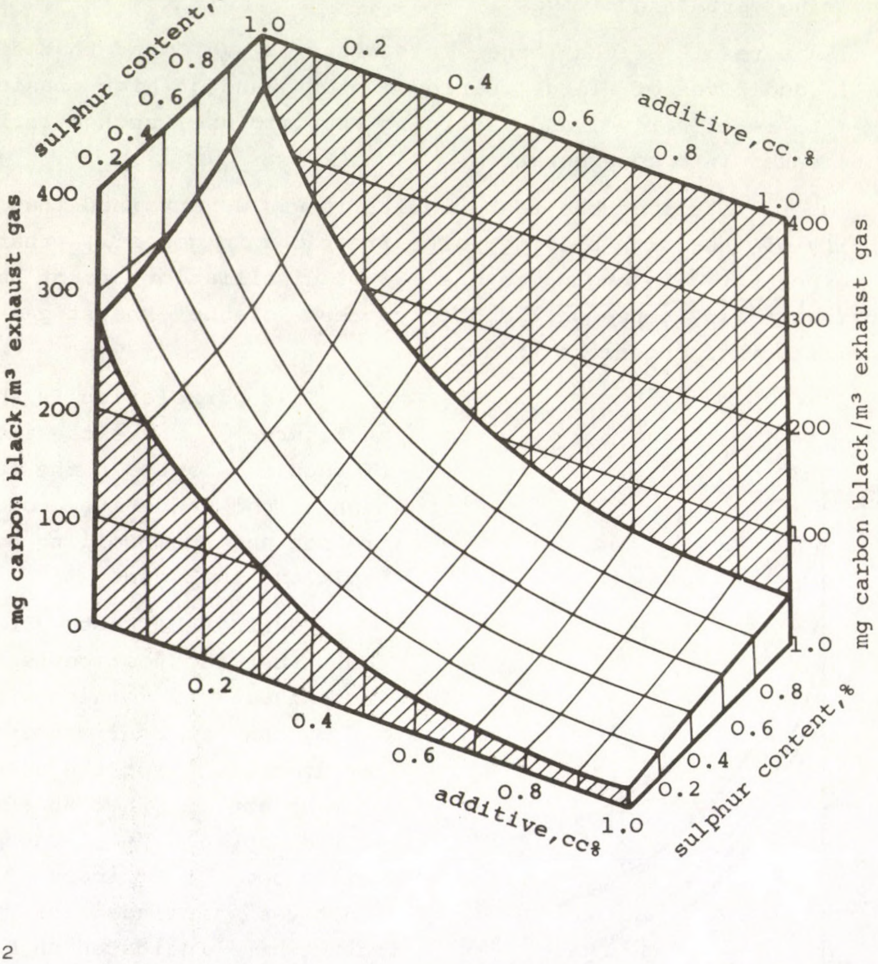

Fig.2

As a trial of the carburation coking model, laboratory tests were carried out on the "Panel Coking" equipment and it was found that under the known carburating temperature conditions of Diesel

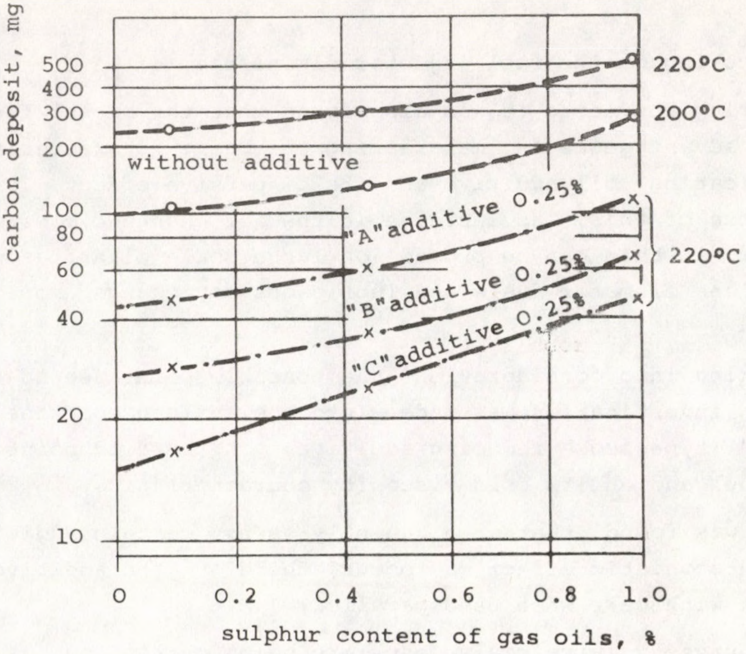

Fig.3

motors, the smoke reducing additives chosen may suppress the degree of sediment formation by an order of magnitude or even completely (Figure 3). The actual effect can be controlled by a long-run plant application test.

Further tests were carried out using additives, which had provided good results in soot reduction, to see the additional effect to be accounted for, during application. In order to answer the question, 150 hour multilateral long-time tests were carried out. On the basis of these tests it can be stated that the use of the additives does not disadvantageously influence the run of the Diesel-motors, in fact they were found to be advantageous in the following:

- reduced wear in the most important structural elements of the motor,

- the degree of deposit decreased on the surface of the piston,

- coking on the fuel injector diminished.

During the tests it was also found that the Diesel fuel additive is advantageous in maintaining the basic characteristic of the lubricating oil additive and its dispersive effect, and as a consequence of this, an increase in the oil change cycles can be expected. If this can be proved on large scale plant tests, the consumption of motor fuels and lubricants may change more favourably.

Taking into consideration the possible point use in the future, an investigation was made into the influence of the "Flow improver" type smoke reducing additives on the cold point of the diesel fuel and on its cold viscosity characteristics.

It was found that when jointly using certain additives a slight antagonistic effect may occur, therefore the additives must be chosen with care when used parallel.

At present large scale tests are being carried out using additives that proved to be suitable in the laboratory tests, on automobiles situated in two garages, to ascertain if the results obtained in the laboratory can be achieved under large-scale conditions. The tests will presumably be completed by the end of this year or the beginning of next year, after which it will be seen whether the use of additives is advantageous, and also if the conditions are provided for introducing the doped oil, mainly in large towns.

Tests have been carried out to produce an organic component of petrochemical origin, which has a high octane number. Trial blendings were carried out on samples produced on a large laboratory scale. This new-composition gasoline was qualified in a full scale motor by the "Europa Test" method. Both the bench and the motorway readings showed favourable results. Consequently a non-leaded gasoline could be produced, with which the discharge of the harmful carbon monoxide and hydrocarbon exhaust gas also proved to be more favourable.

Manufacturing technology and the application of technical tests connected with this are now in progress.

With the increase in the number of different works, an ever increasing quantity - although in small concentration - of hydrocarbons harmful to the environment are getting into the atmosphere, and can be made innocuous to environment most economically by catalytic oxidation [2]. This is especially so when the amount of combustible material is below the ignition concentration. Experiments have been carried out on this for some years in the Institute. A metaloxide catalyst has been elaborated, containing manganese and iron oxide as main components, and alkaline and alkaline-earth metals as promotor [3]. This catalyst has been produced in the laboratory and on a semi-large scale and was tested to find out how different organic materials can be transformed into carbon dioxide, which do not damage the environment. The oxidation of acetaldehyde was examined in detail using this catalyst. This is shown on Figure 4, the catalytic oxidation of methanol on Figure 5, and the catalytic oxidation of benzene vapours is demonstrated on Figure 6. The effect of the temperature and the concentration of the contamining material were tested in the case of all three materials.

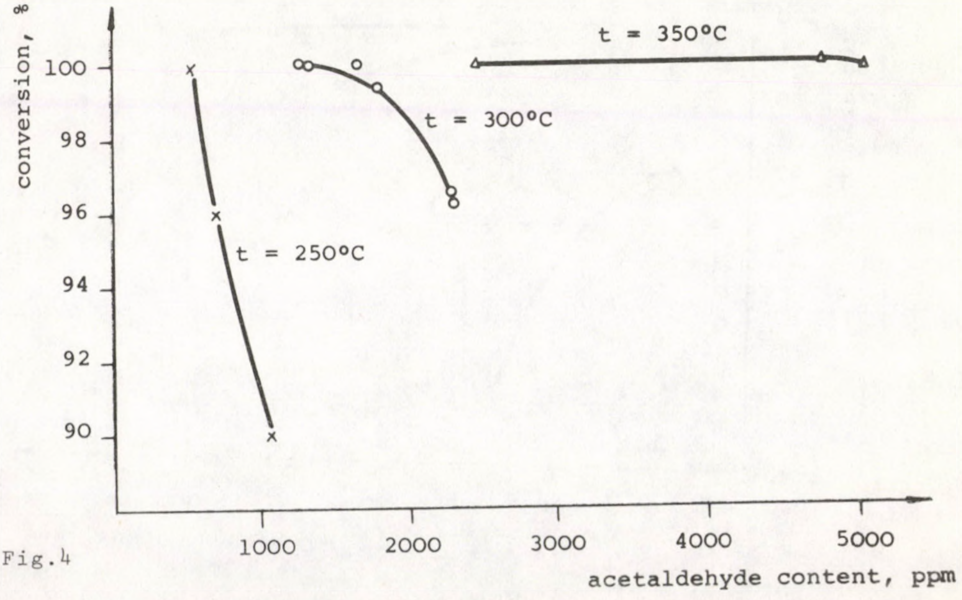

Fig.4

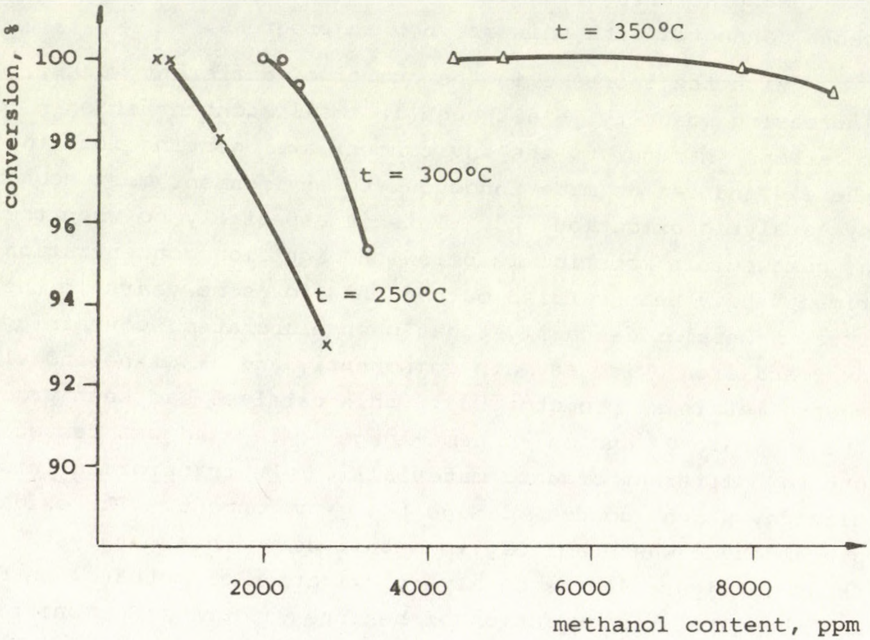
conversion, %
100
98
96
94
92
90
t = 350°C
t = 300°C
t = 250°C
2000
4000
6000
8000
methanol content, ppm

Fig. 5

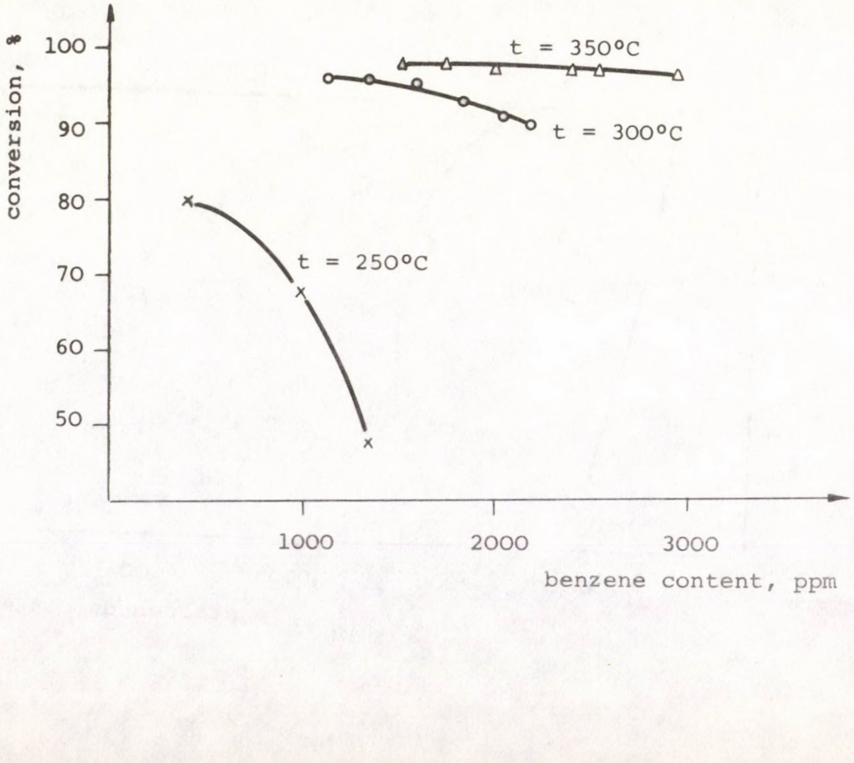
conversion, %
100
90
80
70
60
50
t = 350°C
t = 300°C
t = 250°C
1000
2000
3000
benzene content, ppm

Fig. 6

The tests undoubtedly show that using the suitable amount of catalyst, at a temperature between 300-400 °C the examined materials can be transformed with a good conversion to carbon dioxide.

The activity of the catalyst was tested, beside the above, in connection with the burning of different plasticizers and plasticizing mixtures. On the basis of the test results obtained, semi-large scale equipment was designed, which is outlined in Figure 7. The results gained from the semi-large scale tests confirmed those attained in laboratory.

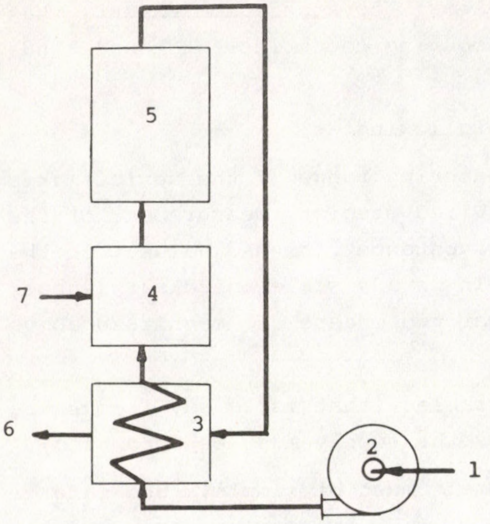

Fig.7. 1 - Input of the air to be purified
2 - Ventilator
3 - Heat exchanger
4 - Preheater
5 - Reactor
6 - Output of purified air
7 - Preheater

Concerning the catalyst, it is essential to mention that an after-burning device has been working for 2 years, which does not serve to burn chemical end gases, but the end gases arising from coffee roasting. The activity of the catalyst during this test period has not lessened. At present the designing and construction of a small plant serving to after-burn gases with high plasticizer content is in progress in a plastic-processing factory.

One of the results achieved by the Institute in the research work connected with the development of test methods and equipment was the elaboration of two portable measuring devices, which together can be used or can be made suitable with certain modifications to measure the concentration of several organic and inorganic air pollutants [4, 5]. The "Sulphodet" device operates on the principle of electron capture and makes it possible to measure the sulphur containing contaminators. The other type of device, the

"Carbodet" works with a flame ionization detector and measures organic air contaminators.

When constructing these devices, stand points were taken into consideration, according to which the constructed devices are able to meet those demands, at least to a certain extent, that arise in Hungary and in the neighbouring countries for these kinds of control instruments.

These stand points are the following:

- the lower limit of the measuring range of the device makes it possible to ascertain the required precise measurement of the permitted maximal concentration substance (the MAC value) of the contamination of the work site. It is advisable to take the upper limit of the measuring range one or two orders of magnitude above this;

- the device must be portable (that is to say it must be suitable in both size and weight), the supply must be automatic;

- the handling of the equipment must be simple, and safe in operation.

The manufacture of these two devices commenced in Hungary, this year.

The further aim of the present research work is to elaborate types of equipment suitable for sited, continuous operation, with the help of which industrial processes and technologies endangering the cleanliness of the atmosphere can be controlled more efficiently.

In addition to those mentioned, experiments have been and are still being carried out to remove hydrocarbons from polluted water, discharged by the various different plants of the oil industry and petrochemical plants. This removal is made in such a rapid and effective way, that the waste water can be treated with the known contaminated water-cleaning equipment [6, 7].

Test showing favourable results are being carried out in the Institute to embed radioactive isotopes and different chemical toxins [e.g. arsenium] into bitumen.

It can be seen that these assignments take up a considerable research capacity. These types of problems, however, are apt to increase in the future and this is why preparations must be made in time to solve them.

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F.R.G.:	20 32280/70
Netherlands:	70. 09664

РЕЗЮМЕ

В статье дается информация о научных исследовательских работах проводимых в области охраны окружающей человека среды, а также о результатах достигнутых в ходе этих работ. Публикуются подробные данные об испытаниях в области снижения выпуска дыма дизельными двигателями, где при помощи использования разных присадок, по результатам испытаний, содержание сажи в выхлопном газе снизилось более чем на 50% . Кроме этого кратко изложены результаты испытаний проводимых в области сокращения содержания свинца в высокооктановых бензинах.

Следующая часть статьи занимается катализаторами разработанными с целью досжигания органических примесей в промышленных конечных газах, разделение которых экономически не выгодное. Дается информация о результатах достигнутых при использовании этих катализаторов в полупроизводственном масштабе. При этом рассмотрено определение оптимальных условий, необходимых для каталитического досжигания различных веществ.

В конце статьи автор сообщает о разработке в институте прибора, предназначенного для быстрого и надежного определения отдельных загрязняющих окружающую среду органических и неорганических компонентов, а также о результатах использования прототипа этого прибора.

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RESEARCH-WORK ON THE PROCESSING OF ROMASHKINO FUEL OIL RESIDUE

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The Hungarian Oil and Gas Research Institute has been working on the processing of Romashkino fuel oil residue from the early 1960s utilizing domestic oil resources. This paper briefly summarizes some of the important results obtained in this field over the past 13-14 years, and mainly deals with the results of technological research-work.

From the 1960s onwards significant changes could be observed in the quantity and composition of the domestically processed oils. The processing of the Romashkino oil imported in increasing quantity from the Soviet Union made it necessary to work out processing technology that was best suited to domestic requirements and the development plans the oil processing industry.

From the very beginning, the Institute joined in the task of processing the Romashkino oil. During the past 13-14 years, in co-operation with the OKGT, DKV and KKV, the Institute solved a number of technological, unit operational and application problems, and developed several processes and products.

1. Processing of Romashkino Fuel Oil Residue

The aim of the Institute's initial research was to establish the type and yield of products obtainable from the Romashkino residue by applying the classical processing procedure shown in Figure 1. In these experiments the aim was to produce the largest possible stocks of motor oil and residual oil. Therefore, during vacuum distillation, products coming within the boiling ranges of spindle oil and motor oil distillates were not separated.

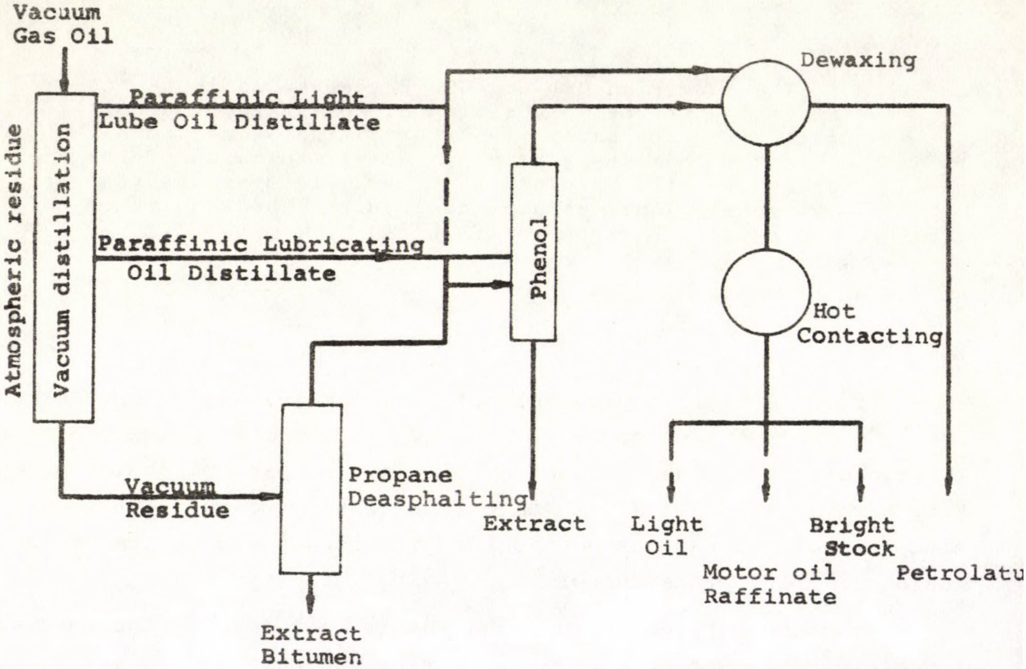


Fig.1. Classical processing of Romashkino residue

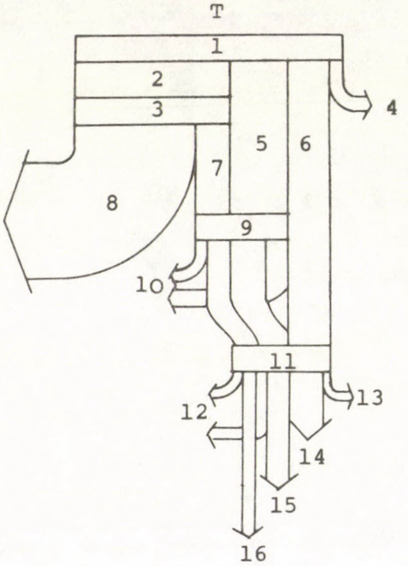
At that time, the oil stocks and residual oils applied in our experiments were produced at the vacuum distillation plant of the Szőny Oil Industrial Company. Table 1 shows the characteris-

Table 1. The characteristics of vacuum distillation products obtained from 52 % atmospheric residue

Property	Residue	Paraffinic oil		Bitumen
		Light	Heavy	
Yield per crude, %	52.8	8.2	11.8	30.1
Yield per residue, %	-	15.8	21.3	57.5
Density at 20 °C	0.9540	0.8887	0.9193	1.008
Refractive index at 70 °C	-	1.4765	1.4946	-
Viscosity, cSt				
at 20 °C	-	21.40	-	-
at 50 °C		7.56		
at 100 °C	32.1	-	9.17	-
Conradson number, %	8.8	0.03	0.38	18.6
Pour point, °C	+3	+10	+37	
Flash point (Marcusson), °C	-	175	254	-
Paraffin content, %	-	8.0	12.1	2.0
Asphalt content, %	-	-	-	5.0
Ash content, %	-	0	0	0.075
Softening point, °C	-	-	-	44
Penetration at 25 °C	-	-	-	220
Ductility at 25 °C, mm	-	-	-	1,000
Molecular weight	-	272	406	-
Ring analysis				
C_A	-	19.3	19.4	-
C_N	-	22.9	18.2	-
C_P	-	57.8	62.4	-
R_A	-	0.62	0.9	-
R_N	-	0.85	1.15	-
Elemental composition				
C %	-	85.50	85.20	-
H %	-	12.50	12.20	-
S %	-	1.89	2.04	3.28

tics of the products obtained during the first series of plant experiments. Paraffinic distillates (consisting of 8.2 wt.% light and 11.8 wt.% heawy distillates) were obtained from the 52 wt.% of atmospheric residue. Both distillates had comparatively low viscosities, whereas the vacuum distillation residue was a bitumen and had a softening point of 44 °C and a penetration of 220 1/10 mm at 25 °C.

In both the laboratory and plant experiments, the vacuum distillation residue was deasphalted with propane, the residual oil and heavy paraffinic distillate were solvent-refined with phenol and the raffinates were dewaxed. The refined products were finally submitted to heat contacting and acid treatment.



T - Top residue
1 - Vacuum distillation
2 - Residue
3 - Propane
4 - Gas oil
5 - Heavy paraffinic distillate
6 - Light paraffinic distillate
7 - Residual oil
8 - Extract bitumen
9 - Phenol
10 - Extracts
11 - Methyl ethyl ketone
12 - Petrolatum
13 - Crystalline slack wax
14 - Spindle oil
15 - Motor oil
16 - Bright-Stock

Fig.2. The material balance for the processing of the Romashkino crude

Figure 2 shows a mass balance illustrating the results of the studies performed on the processing of Romashkino oil. The dewaxed oil with a viscosity of 7.7 cSt at 50 °C and a pour point of -13°C produced from the light paraffinic distillate (6) may be used as spindle oil. The raffinate (15) of a yield of 7.8/wt % oil, viscosity index of 80, viscosity of 43.9 cSt at 50 °C and pour point of -10 °C produced from the heavy paraffinic distillate (5) with a viscosity of 9.17 cSt at 100 °C and Conradson number of 0.4 wt % belonged to the motor oils then used in Hungary. In addition to the raffinate (16) with a viscosity index of 81, a yield of 3.4/wt % oil and a pour point of -10 °C produced from the deasphalted oil (7) under optimal conditions, a bright-stock was obtained with a viscosity of 22.3 cSt at 100 °C. The motor oils and bright-stock possessed suitable properties and therefore met the requirements of those days.

2. The Production of High Viscosity Oils

From these initial experiments it was observed that under the said conditions of vacuum distillation and propane deasphalting, motor oil stocks with a viscosity higher than 40-45 cSt at 50 °C can be produced only by mixing with bright-stock and motor oil having a viscosity of 40-45 cSt.

According to the previous Soviet literature and the own research, motor oils of higher viscosity cannot be produced by distillation as the required distillates contain a high quantity of resinous materials. At the same time, the production of bright-stock is considerably expensive due to the comparatively high refining losses, the circulation of a large quantity of propane and the high yields of paraffins.

Therefore, it was justified to consider which are the most suitable and economical procedures by which the possibilities of preparing high viscosity products could be widened.

Research work was carried out in two directions:

1. The possibility was examined of preparing from the Romashkino residual oil, vacuum residue with yields of 25 and 20 wt % instead of 30 wt % and the conditions for refining the recovered heavy oil destillate and the properties of the product obtained.

2. The possibility was examined of improving the economic feasibility of propane deasphalting.

From the examination of the first problem, it appeared that through an appropriate method of operation, in addition to bitumen with a softening point of 55 °C and yield of 20 wt %/oil, heavy distillate having a yield of 8.3 wt %/residue, a viscosity of 20 cSt at 100 °C and a Conradson number of 2 wt % was obtained which could be refined in phenol with no special difficulty. The raffinates obtained in this way are characterized by the example shown in Table 2.

Table 2. The characteristics of the oil raffinate obtained from the refining of Romashkino heavy oil distillate

Yield per atm. residue, wt %	5.7
Density, d_4^{70}	0.8962
Viscosity	
cSt/37.8 °C	210.98
cSt/50 °C	106.50
cSt/98.9 °C	15.80
cSt/100 °C	15.13
V.I.	81
Pour point, °C	-12
Conradson number, %	0.40
Flash point, °C	275
Oxidation stability, V_2/V_1	1.5
C_2-C_1	1.7

It can be seen that in this manner, a product with a viscosity index of 80, and pour point of -12 °C, a viscosity of 15 cSt at 100 °C can be obtained, whose yield is 5.7 wt % per atmospheric residue. Contrasting this with the product having a viscosity of 23-24 at 100 °C, similar viscosity index and pour point, a yield of about 8 wt % obtainable from the propane deasphalting of 30 % petroleum tar, it become obvious that the preparation of heavy oil distillate, whilst leaving out the deasphalting operation, ensures that high viscosity components of valuable lubricating properties are withheld in the bitumen.

However, it was worth while to deal with the second problem which concerns the improvement of the economic feasibility of the propane deasphalting process.

In one instance, a heavy distillate with a viscosity of 20 cSt at 20 °C was mixed with the 30 % vacuum residue in 4:1 ratio and the mixture thus obtained was submitted to propane deasphalting. The result was that while in the case of pure 30 % vacuum residue, deasphalting the quantity of material to be deasphalted per unit amount of end-raffinate was sevenfold, this procedure ensured a sixfold ratio only. However, it is true that the yield of obtainable end-raffinate of a viscosity of 21 cSt at 100 °C, viscosity index of 84 and pour point of -12 °C per atmospheric residue was less by 25 %, while, at the same time, the output of the propane deasphalting plant could be raised by 40 % with this procedure.

By another method, the propane deasphalting could be carried out in two steps, and so three products could be obtained, namely residual oil, resin and bitumen. Table 3 contains some of the important characteristics of this procedure, using 30 % Romashkino vacuum distillation residue. By applying a volume ratio of 1:6 of basic material and propane in the extraction column (1), the overhead products were oil and resin, obtained together and the bottom product was bitumen. The overhead products, a propane solution of oil and resin, were passed into column (2) where they met a further volume ratio of 1:2 of basic material and propane, and residual oil as overhead product and resin as the bottom product were obtained. The quantity of residual oil obtainable from the two-column technology equalled the yield obtained from the classical single column technology, whilst in addition to the residual oil 13 wt % of the resin was recovered.

Table 3. Two-column propane deasphalting of Romashkino vacuum residue

Main plant characteristics of the process

1. column top temp.	56 - 58 °C
2. column bottom temp.	48 - 51 °C
1. column top temp.	82 - 84 °C
2. column bottom temp.	69 - 71 °C

Material balance data, wt %

	Feed	Oil	Resin	Bitumen	Loss
Per raw material fed in	100.0	29.4	12.6	51.2	6.8
Per residue	53.3	15.7	6.7	27.3	3.6
Per crude	30.8	9.1	3.9	15.8	2.1

Characteristics of the products

	Oil	Resin	Bitumen
Viscosity at 100 °C, cSt	28	113	-
Conradson number, wt %	1.3	5.4	-
Softening point, °C	-	-	80
Penetration at 25 °C, 0.1 mm			6

3. Utilization of the Resin Recovered from the Vacuum Distillation Residue

For research-work on the utilization of the resin obtainable from the two-column technology, two sides of the problem were considered.

In co-operation with the NAKI, a procedure was developed in which the resin was hydrogenated, solvent-refined and dewaxed, and depending on the refining conditions, in addition to a yield of 50-80 %, oil raffinates having a viscosity of 15-25 cSt at 100 °C and viscosity index of 80 could be produced.

In co-operation with DKV, NyKV and the Hungarian Cable Works another process was developed in which good quality cable insulating material was produced from the resin in the absence of a propane solution of polymeric or pine gum, but with the help of acid treatment and decolorization performed under the suitable conditions. From studies of the production and cable impregnation processes performed at plant level, resins having viscosities of 60-140 cSt at 100 °C and Conradson numbers of 4.5-5.5 wt %, were chosen as the raw material for the cable insulator.

Table 4. Properties of cable insulating materials

Viscosity, cSt	
at 80 °C	98 - 200
at 100 °C	47 - 80
at 140 °C	14 - 19
Density at 70 °C	0.898 - 0.912
Sulphur content, wt %	1.8 - 2.2
Pour point, °C	+40 - +48
Frass break point, °C	under -30
Acid number, mg KOH/g	0
Ester number, mg KOH/g	0
Dielectric loss factor at 100 °C	10×10^{-4}
Specific resistance at 100 °C Ohm·cm	$1.1 \times 10^{13} - 2.0 \times 10^{13}$

Table 4 shows the characteristics of the insulator prepared from the resin having a viscosity of 59.5 cSt - 147 cSt at 100 °C.

Application studies proved that the quality of cable insulators obtained with this process equalled that of foreign produced insulators.

4. The Preparation of Industrial Oils from Romashkino Light Paraffinic Distillate

In addition to the research-work on the processing of the Romashkino vacuum distillation residues, laboratory, semiplant and plant experiments were simultaneously carried out on the processing of light paraffinis distillates boiling between 290-405 °C into industrial oils. Dewaxing experiments were carried out in acetone-benzene-toluene solvent on these distillates. The aim of these studies was the establishment of the relationship between the most important operation parameters of dewaxing, such as the optimal solvent composition, the maximum acetone content, the required amount of wash liquor, the sharpness of separation and the properties of the products.

Here those studies are mentioned which helped us in establishing the production technology of transformer oil from the Romashkino oil.

In the preparation of transformer oil from the paraffinic oils, first and foremost, the establishment of the required low pour point, low cold viscosity and sufficient gas stability was the main problem. To solve this problem two methods were considered.

a) dewaxing at low temperature of 40-50 °C, or

b) lower degree of dewaxing followed by the application of additives for the improvement of pour point and gas stability.

Considering our domestic resources, the latter method was chosen.

In this case, the pour point depressant had to meet a number of requirements. Obviously, in addition to improving the low viscosity characteristics, it should not damage the dielectric constants of the oil, during the application of the doped oil, pour point reversion should not take place and the additive, under the transformer conditions, should not spoil.

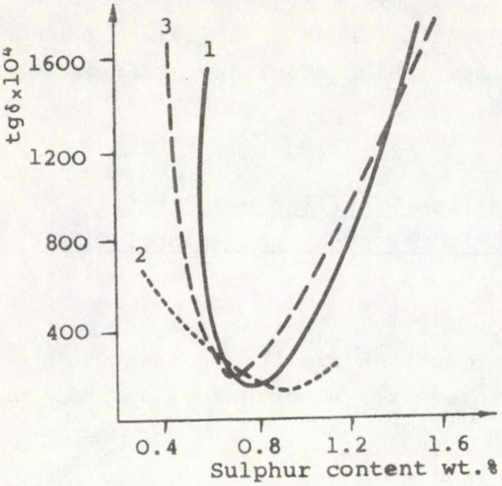


Fig.3. The electrical loss factor and sulphur content of the transformer oil produced from oil of various boiling point ranges

1. Basic oil boiling point range: 300-400°C
2. Basic oil boiling point range: 300-350°C
3. Basic oil boiling point range: 350-400°C

From our production and application studies, both at laboratory and pilot plant level, it was established that by choosing the suitable pour point depressant of the polimeric type, these requirements could be fulfilled. From these studies it was ascertained that in the case of Romashkino basic materials of high sulphur and resin content, the suitable oxidation stability of the transformer oils could be ensured only through solvent refining. The oxidation stability depended to a considerable extent on the boiling point range and the sulphur content of the starting material. From Figure 3 it can be seen that the electrical loss factor measured after the oxidation study shows an optimum as a function of the sulphur content of the transformer oil. The optimal point is a function of the boiling point ranges of the starting distillate. If the product boils at a temperature between 300-350 °C, the optimal sulphur content is 0.8-1.0 wt %, but if the boiling point range of the transformer oil is 350-400 °C its sulphur content is 0.6-0.8 wt %.

As for the gas stability, the transformer oils were expected to be gas acceptors. As is well known, transformer oils from naphthenic oils are strong gas acceptors, whilst products from paraffinic sources are gas donors. It was established that Romashkino transformer oils prepared under the correctly chosen conditions satisfied the requirements with regard to the above fact.

Application studies were carried out on the transformers, using - since 1967 - transformer oils containing a combination of pour point depressants and inhibitor-passivators prepared according to our procedure. The results have - so far - proved that the production of high quality, high stability transformer oils from Romashkino was feasible.

5. The Preparation of Microcrystalline Paraffins and Paraffin Products of Special Properties from Romashkino Residual Oil Petrolatum

In the course of lube oil production from the Romashkino oil of high paraffin content, side-products, slack waxes, as well as heavy oil and residual oil petrolatum containing various macro and microcrystalline paraffins were obtained. Therefore, the possibilities of producing macro and microcrystalline paraffins and their quality were studied in detail.

On the basis of the laboratory and pilot plant experiments it was concluded, for example, that by solvent deoiling of the Romashkino residual oil petrolatum, raw microcrystalline paraffin with a yield of 40-45 wt % could be prepared, which fulfilled Hungarian standard requirements. It is inte-

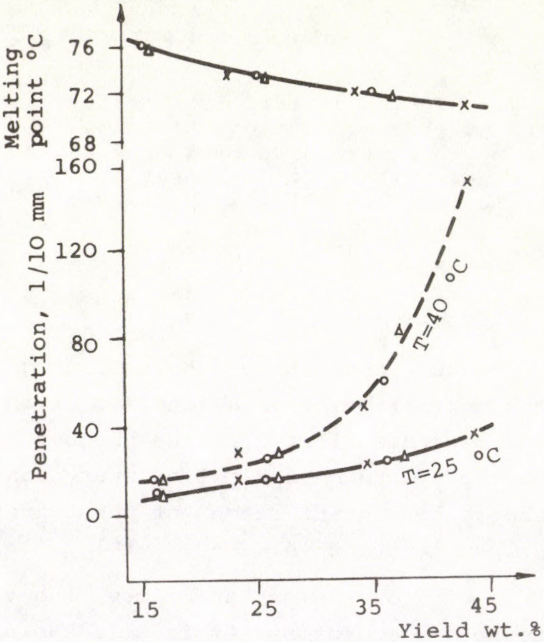


Fig. 4. Relationship between the important characteristics and the yield of microcrystalline paraffins. x MEK, o MiBUK; Δ MnPK

resting to note that a product with a pour point of 75 °C, penetration of 12-13 1/10 mm and a yield of 20 wt % was recovered. The sulphur content of the product having a pour point of 76 °C and containing 0.5 wt % of oil was 0.16 wt %.

Figure 4 shows the penetration measured at 25 °C and 40 °C and the pour point of the microcrystalline paraffins as a function of the paraffin yield. From these facts it appears that for almost equivalent separation efficiency, separation sharpness and a given pour point, there was a penetration value which - in accordance with the given paraffin yield - depended to a small extent, on the type of solvent and temperature of deoiling. Figure 5 shows the selectivity of the solvents expressed in changes of pour point and penetration values as a function of solubility. From these results, it is clear that for a given solubility value, i.e. paraffin yield, there is a corresponding selectivity value which hardly depends on the type of solvent.

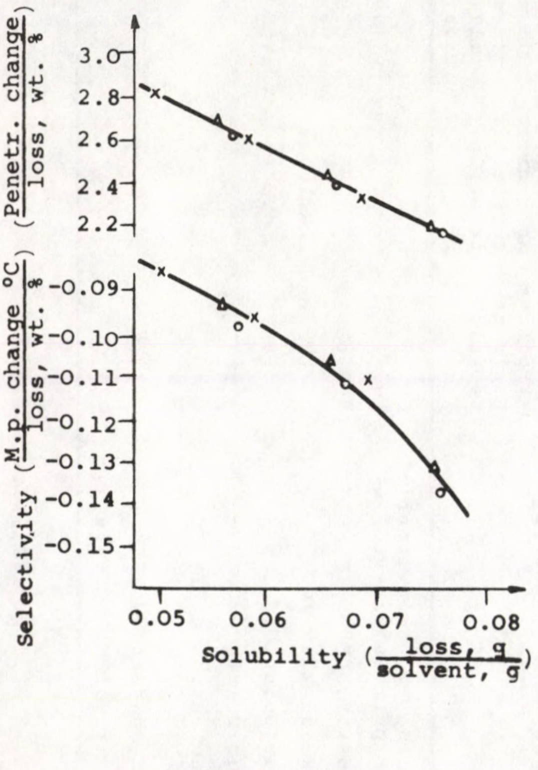


Fig.5. Relationship between selectivity and solubility
x MEK, MnPK, o MiBUK

The fractional crystallization of the residual oil petrolatum of Romashkino origin was also studied in detail.

Table 5 summarizes the conditions of fractionation performed at +30 °C and +10 °C, and the characteristics of the products obtained. From the results,

Table 5. Stage I of two-stage laboratory fractional crystallization of petroleum from residual oil

Preparation of hard microcrystalline paraffins at +30 °C and + 10 °C
Conditions of experiments:

Separation temp., °C	+30 and +10 °C
Solvent composition, vol.%	
MEK	70
Benzol	30
Quantity of diluting solvent, wt %	700
Quantity of wash liquor, wt %	400

Products & Properties	Residual oil petrolatum (basic material)	obtained at +30 °C		obtained at + 10 °C	
		Hard microcrystalline paraffin	Oil and soft microcrystalline paraffin	Hard microcrystalline paraffin	Oil and soft microcrystalline paraffin
Yield per basic material per petrolatum, wt %	100	22.1	77.9	55.0	45.0
Density, d_4^{80}	0.8264	0.7953	0.8360	0.8065	0.8535
Viscosity at 100 °C, cSt	12.43	10.18	13.52	10.50	16.92
Pour point, °C	65.5	78.2	+45	70.5	22
Drop point, °C	67	78		70.7	
Penetration at 25 °C 0.1 mm, MSZ 13 162	144	9		33	
Oil content, wt %	23.78	1.0		6.65	
Break point, °C (Fraas)	-29	above +22		above +22	

Table 6. Stage II of two-stage laboratory fractional crystallization of petrolatum from residual oil

Preparation of soft microcrystalline paraffins from the filtered oil at +30 °C in stage I

Conditions of experiments:	
Separation temp., °C	-20, -10 and ±0
Solvent composition, vol.%	
MEK	70
Toluene	30
Quantity of diluting solvent, wt %	400
Quantity of wash liquor, wt %	700

Products & Properties	Soft microcrysatalline paraffins		
	at -20 °C	at -10 °C	at ±0 °C
Yield per basic material (petrolatum), wt %	43.5	37.0	31.1
Density, d_4^{70}	0.8174	0.8128	0.8106
Viscosity, at 100 °C, cSt	10.62	10.38	10.12
Pour point, °C	50.4	52.5	53.2
Drop point, °C	50.2	51.8	53.0
Penetration at 25 °C, 0.1 mm (MSZ 13162)	96	57	33
Oil content, wt % (ASTM)	5.18	1.30	0.51
Break point, °C	under -30	-30	-26

it was possible to establish that between +30 - +10 °C and for oil content of 1.7 wt %, hard microcrystalline paraffins having a pour point of 70-78 °C could be recovered, whose penetration, at 25 °C, depending on the oil content, varied from -10 - 30 1/10 mm.Table 6 shows the characteristics of soft mycrocrystalline paraffins prepared in the second stage from the filtered oil at +30 °C. Clearly, products prepared at 0 °C and -10 °C have high plasticity at low temperatures, their break point is -26 and -30 °C respectively. Their penetration for oil content of 0.5-1.5 wt % does not surpass the value allowed in the standard requirements for paraffin products.

Taking into consideration the yield of hard microcrystalline paraffins obtained in stage I, 52-60 wt % of petrolatum was processed into valuable microcrystalline paraffins of special properties in both stages.

The products obtained at -20 °C from the oil prepared at +30 °C had plastic properties, however, their break point was below -30 °C, and because of their high penetration value, their application, in the absence of additives, was limited.

For years we have been studying the preparation of paraffin products of the special properties that fulfilled the utilization requirements of such industries as paper, household chemical and foodstuff manufacturing.

In the course of this research, the studies included the doping of macro and microcrystalline paraffins with polyethylene, polyisobutylene and ethyleneacetate copolymerics, the compounding of macrocrystalline paraffins with mycrocrystalline paraffins and the three-component systems consisting of macrocrystalline and microcrystalline paraffins, as well as additives. In this manner, a complete series of paraffins of special properties could be obtained. Two diagrams illustrate this fact. Figure 6 shows the penetration at 25 °C and viscosity at 140 °C of the systems consisting of microcrystalline residual petrolatum having an oil content of 8 wt % and a pour point of 53 °C and polyethylene wax having a viscosity of 1029 cSt at 140 °C and pour point of 97 °C as a func-

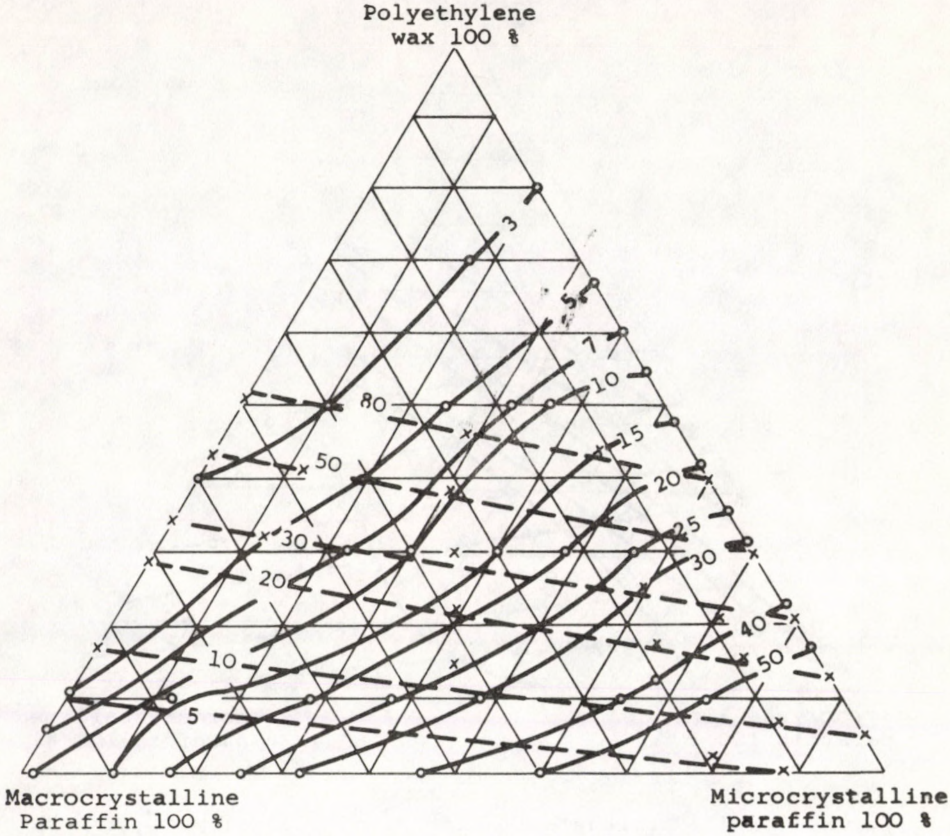


Fig.6. The penetration at 25 °C and viscosity at 140 °C of the three-component systems. —— Penetration; --- Viscosity

tion of composition. Figure 7 shows the tensile strength at 25 °C and viscosity at 140 °C of the same products.

On the basis of our laboratory and pilot plant production and application experiments, we processed a complete series of pa-

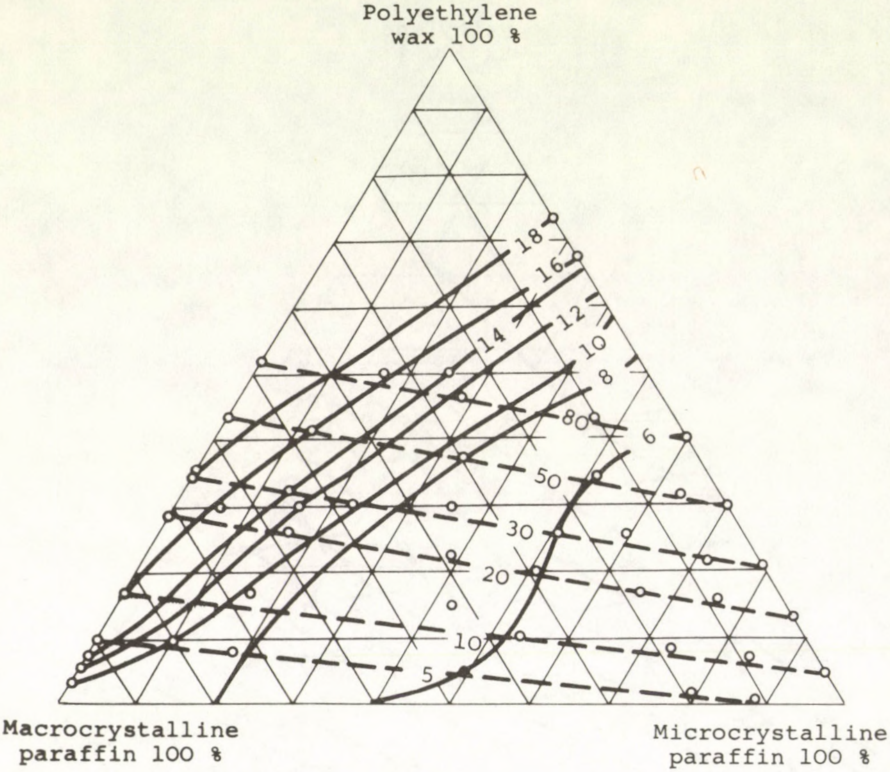


Fig.7. The tensile strength at 25 °C and viscosity at 140 °C of the three-component systems. —— Tensile strength at 25°C for a pulling velocity of 50 mm/min.;--- Viscosity at 140°C

raffin products applicable in the paper, household chemical and foodstuff industries, and their full-scale production was realized by the Nyirbogdány Oil Company.

The research on paraffins from the Romashkino crude oil also involved the refining of the paraffins. For the refining of liquid (at room temperature) and macrocrystalline paraffins, a process was developed which involved the regeneration of the silica gel adsorbent, that was essentially based on the frontal chromarography and was realized at pilot plant level. The extract rich in aromatics was washed down the adsorbent column with the help of a solvent consisting of acetone, toluene and benzene. The silica gel charge was regenerated first by blowing with superheated vapour, then hot air. The regenerated silica gel could then be applied in the next cycle of refining.

6. The Preparation of Bitumens from Romashkino Basic Materials

DKV produces extract bitumen by the distillation and oxidized propane deasphalting of a large amount of Romashkino crude.

The earlier domestic bitumen production was based on the processing of the Nagylengyel crude oil. Therefore in the 1960s it was found necessary to improve the quality of bitumens preparable from the new raw material, develop the required technological procedures for the realization of the given quality and the suitable conditions for production.

The fruits of this work could be essentially summarized as follows: it was confirmed that given the suitable chosen Romashkino residual oils, extract bitumens obtained by propane deasphalting, extracts from lube oil refining and heavy oil distillates; furthermore by mixing all these and applying an intensive oxidation technology, a product of 82/85, according to the national standardized and DIN quality requirements, could be obtained. Deviations from these requirements were, in practice, insignificant and occurred only in some products, especially in their paraffin value.

The work performed in this field and its results could constitute an article of its own. Here two tables only are presented. In Table 7 the characteristics of those materials are summarized whose application made the production of bitumens of the aforementioned qualities possible. Table 8 shows the production possibilities of two types of bitumen which fulfill the NM-130 and DIN 82/85 quality requirements.

Table 7. Basic materials for the production of Bitumens

	Light petr. tar	Petr. tar	Heavy Petr. tar	Extract bitumen	Heavy paraffinic distillate	Residual oil extract
Softening point, $^{\circ}$C	43 - 44	46	48	60	-	-
Penetration at 25 $^{\circ}$C, 0.1 mm	180 - 280	158	114	17	-	-
Ductility, at 25 $^{\circ}$C, mm	770 - 1,000	950	above 1,000	above 1,000	-	-
Break point, $^{\circ}$C	-17 -19	-16	-11	+10	-	-
Paraffin content. wt %	2.2 - 2.5	2.3	2.2	1.8	-	-
Asphalt content. wt % (ether)	8 - 10	11	12	13	-	-
Flash point, $^{\circ}$C (Marcusson)	-	-	-	-	247	286
Viscosity at 100 $^{\circ}$C, cSt	-	-	-	-	10.7	39.4
Pour point, $^{\circ}$C					+39	+30

Table 8. Production possibilities for NB 130 and 85/25 quality requirements

Product			Possible raw materials	Method of preparation
Symbol	Its properties			
NB-130	Softening point, °C	43-49	Light petr. tar	Oxidation
	Penetration at 25 °C, 0.1 mm	110-160	Petr. tar Heavy petr. tar	Oxidation Oxidation
	Break point, °C, max.	-10	70 wt % extract bitumen + 30 wt % residual oil extract	Mixing + Oxidation
	Ductility at 25 °C, mm, min.	1,000	80 wt % extract bitumen + 20 wt % residual oil extract	Mixing
DIN 85/25	Softening point, °C	80-90		
	Penetration at 25 °C, 0.1 mm	20-30	80 wt % light petr. tar + paraffinic distillate	Oxidation
	Break point, °C, max.	-10	80 wt % light petr. tar + 20 wt % residual oil extract	Oxidation
	Ductility at 25 °C, mm, min.	30		
	Paraffin concent., wt % max.	2		

7. Intensification Research on the Processing of Romashkino Fuel Oil Residue

Finally it should be mentioned that in co-operation with the DKV - which processes the Romashkino fuel oil residue - an examination was made of the intensification of some of the unit operations of the company's lube oil block. In this respect, numerically expressible technical and economic results were obtained with the propane deasphalting and phenol refining plant and at present an examination of the distillation plant is being carried out.

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In this report, an attempt was made to summarize nearly two and a half decades of research activities by mentioning a few results, in which efforts were made to assist the solution of important development problems and work out a technology for the processing of the Romashkino fuel oil residue. Considering the results applied in industry, research reports dispatched to industry, reports delivered at scientific conferences both in Hungary and abroad, and patents based on some of our processes, it is felt that the work in this field was successful.

Acknowledgement is made to the role played in this research work by our colleagues at the Oil Department. The research work was planned and carried out by Dr. Endre Vámos, István Kádár, Dr. Miklós Magyar, Mrs. L. Földes, Ferenc Simon, Sándor Börzsönyi, Dr. Mihály Kristóf, Mrs. M. Fényi, Mrs. E. Kántor, József Szirbek and Dr. Gyula Major.

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РЕЗЮМЕ

Венгерский Научно-Исследовательский Институт Нефти и Природного Газа, принимая во внимание возможности отечественной нефтяной промышленности, с 1960 года занимается вопросами использования ромашкинской смолы. Сообщение содержит важнейшие результаты достигнутые в исследовательской работе названной области за последние 13-14 лет. Не стараясь на подробное изложение, работа содержит результаты прежде всего технологических исследований.

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PRODUCTION OF OLEFINS BY THERMAL CRACKING OF LIQUID HYDROCARBONS

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The authors review some important and directly utilizable results of the research work on pyrolysis carried out at the Hungarian Oil and Gas Research Institute. Apparatuses and experimental methods are briefly described. The most important results of the pyrolysis of individual hydrocarbons, hydrocarbon mixtures and naphta fractions, as well as the method elaborated for the calculation of yield pattern are outlined. Results obtained in different reactors are compared and evaluated. On the basis of experiments carried out with various naphta cuts, the effects of feed composition and operation conditions on yield patterns are demonstrated.

INTRODUCTION

The preparation of olefins by pype-still pyrolysis of the various hydrocarbon fractions is one of the most important branches of the production of chemical industrial basic materials.

With regard to the national development plans, the Institute started research work in 1964 on the pyrolysis of hydrocarbons. In the first few years, in addition to the development of pyrolysis equipment and procedures, the authors were mainly engaged with the problems of establishing and installing an ethylene plant at the TVK with a capacity of 25,000 tons/year. In recent times, they studied the complex process of gasoline pyrolysis, the effects of the quality of raw material and the pyrolysis conditions on the product distributions and the obtainable yield patterns in connection with the planned olefin plant with a capacity of 250,000 tons/year as requested by the NIM Technical Development Department.

Despite the fact that the output of the ethylene plants so far established is about 20-25 million tons a year, surprisingly limited and sketchy information is available in literature on the pyrolysis process and the determination of the optimal operation conditions for the plants [1-7]. Such information was considered top-secret know-how by the companies that manufactured and transported the plants, and was only partially accessible. For an olefin plant to be economical, and given the type of raw material as well as its optimum operation for the required products, it is necessary to known the basic pyrolysis process.

In this report the aim is to give a brief, but comprehensive review of some of the important results directly applicable in practice, which were obtained during the research work carried out at the Institute.

Experimental Equipment and Methods

Tubular reactors of various sizes and capacities were constructed for the research and their important characteristics are shown in Table 1 [8-10]. The laboratory reactor is operated under isothermal and isobaric conditions, but the bench-scale reactor and pilot plant can be operated under temperature, pressure and flow conditions prevailing in the industrial equipment.

Gas chromatographic methods were developed for the detailed analysis of the raw materials and products of the pyrolysis. After separating the products the gaseous and the liquid products were analyzed in columns of three and two different polarities respectively. During the analysis, the concentrations were determined of 40 and 50 components in the gaseous and the liquid samples respectively.

Table 1. The dimensions and characteristics of pyrolysis reactors

Characteristics	Laboratory reactor	Bench-scale reactor	Pilot plant tubular furnace at Pét
Tube diameter, mm	6	6	19
Tube length, m	1.3	24	80
Length of reaction zone, m	0.7	22.7	50-60
Max. feed, kg/h (+50 % water)	0.5	3.5	42
Temp. distribution	isothermal	controllable profile	controllable profile
Heating	electrical	electrical	PB gas
Temp. measurement	along full length	at point 6	at point 7
Pressure conditions	isobaric	non-isobaric pressure meas. at point 6.	non-isobaric pressure meas. at 7
Intermediary sampling	none	at 5	at 7
Flow conditions	laminar (Re = 1,400)	turbulent (Re = 7,000)	turbulent (Re = 26,700)
Pressure drop (max.)	1÷2 torr	2 atm	2.5 atm

In order to process the extraordinarily numerous data Gier electronic computers were utilized, but their evaluation was carried out with the aid of Hewlett-Packard 9100/B and Hunor electronic calculators.

Table 2. The basic materials for pyrolysis experiments

Individual hydrocarbons:	n-hexane	C_6 nP
	2-methyl-pentane	C_6 iP
	2,2-dimethyl-butane	C_6 iP
	cyclohexane	C_6 N
	n-heptane	C_7 nP
	2,4-dimethyl-pentane	C_7 iP
	n-octane	C_8 nP
	2,2,4-trimethyl-pentane	C_8 iP
Binary mixtures:	n-heptane-2,2,4-trimethyl-pentane	
	n-heptane-cyclohexane	
	2,2,4-trimethyl-pentane-cyclohexane	
Ternary mixture:	n-heptane-2,2,4-trimethyl-pentane-cyclohexane	
Sexternary mixture:	n-hexane	
	2-methyl-pentane	
	cyclohexane	
	n-heptane	
	2,4-dimethyl-pentane	
	2,2,4-trimethyl-pentane	
Gasoline fractions:	Romashkino gasoline cut:	60-180°C; d_4^{20} 0.7253
	Romashkino light gasoline:	37-111°C; d_4^{20} 0.6718
	Raffinate:	42-120°C; d_4^{20} 0.6745
	Mixed gasoline:	50-175°C; d_4^{20} 0.7224

The research programme consisted of the pyrolysis of individual hydrocarbons (the main constituents of the gasoline fraction), two, three and six component mixtures of the latter and the various gasoline fractions. Table 2 shows a summary of the properties of the raw materials used in the detailed studies.

Pyrolysis of Individual Hydrocarbons [5, 11-13]

It is known that the product distribution of pyrolysis depends, to a large extent, on the types of the constituents of the gasoline and their structure, but the reported data are very sketchy. In order to examine this problem, pyrolysis of individual hydrocarbons of various types and structures was carried out in the earlier-mentioned reactor with the temperature and residence time ranges of 600-840 °C and 0.1-2 seconds respectively, which are of interest for the given technological processes. The yield data of the main products for identical degree of pyrolysis (at a conversion of 90 %) are shown in Figure 1. It can be clearly seen from the diagram that wide deviations exist between the yield data of the various types of hydrocarbons.

The normal paraffins of varying carbon numbers show similar product patterns, while the yields of ethylene (high), propylene and the unsaturated C_4 hydrocarbons are 34-42 %, 16-18 % and 6-10% respectively.

The product pattern of isoparaffins significantly deviates from the above figures and the isoparaffins of varying structures show a product distribution significantly different from that of one another. In general, the yield of ethylene is low, 5-15 %, that of propylene varies within a wide range, 7.5-29 % and finally that of unsaturated C_4 hydrocarbons, especially the quantity of isobutylene is between 13-38 %.

Cyclohexane and generally naphthenes give a high yield of ethylene of approximately 30 %, the yield of propylene is low while the yield of unsaturated C_4 hydrocarbons is high and a very high yield of butadiene and a large quantity of benzene are obtained.

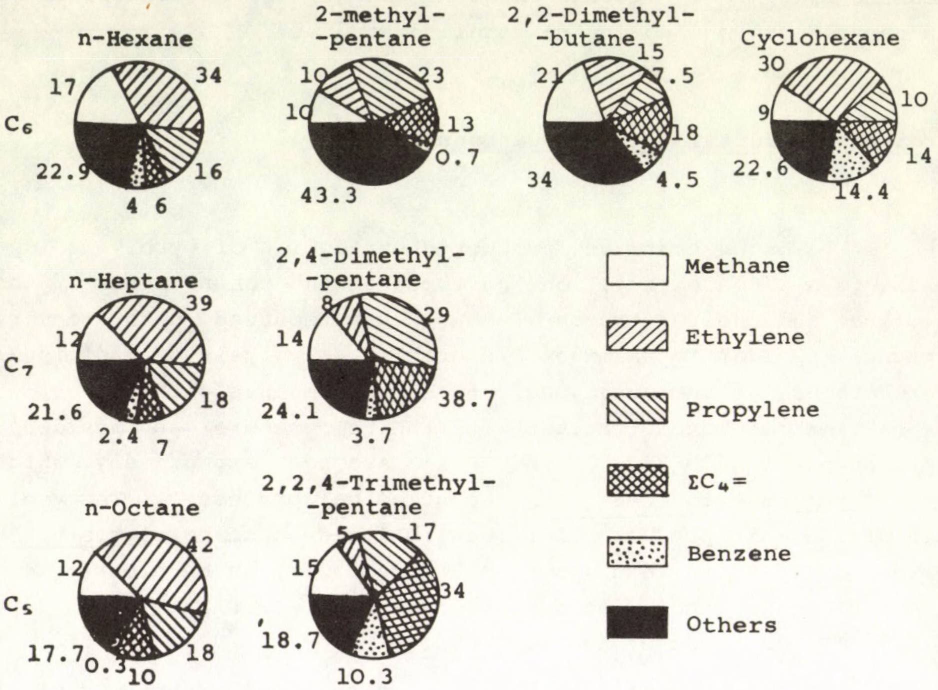

Fig.1. The yield data of the pyrolysis of individual hydrocarbons, in wt % at a conversion of 90 %

The above examples illustrate that the qualitative and quantitative nature of the components of the gasoline has a significant influence on the obtainable yields of the products.

The Pyrolysis of Hydrocarbon Mixtures and Gasoline Cuts [9, 14-17]

The process of pyrolysis was studied on the basis of the pyrolysis of two or three component hydrocarbon mixtures and the various gasoline fractions carried out in the laboratory reactor and the possibility of computing yield data from the information obtained with the pyrolysis of individual hydrocarbons. Various units are used in literature to characterize the conversion of the pyrolysis of hydrocarbon mixtures and gasoline fractions or the severity of pyrolysis process, but a generally accepted and unambiguous characteristic applicable in practice has still to be established.

On the basis of a detailed study of the pyrolysis reactions and the numerous measured data, a new factor was introduced that indicates the degree of the pyrolysis of hydrocarbon mixtures, i.e. the severity of pyrolysis which is termed the degree of decomposition.

Degree of decomposition:

$$X = \sum_{j=1}^{k} y_j x_j \tag{1}$$

The degree of decomposition represents the sum of the conversions, (x_j) of the individual hydrocarbons present in the starting mixture under the given conditions multiplied by the corresponding molar fractions of the starting constituents. In the kinetic equations describing the pyrolysis of individual hydrocarbons the conversion was replaced by the degree of decomposition of the mixture, the equations thus obtained could be directly used in expressing the overall decomposition rate of the mixtures.

Calculation of Yield Patterns from the Yields of Individual Hydrocarbons

It was clear from the pyrolysis experiments performed with model mixtures that the yields of the main products under conditions of technological importance consisted of the sum of the yields obtained in the course of pyrolyzing the individual hydrocarbons contained in the mixture and was a function of the degree of decomposition.

A simplified kinetic model was developed on the basis of the overall kinetic relationships describing the change in the degree of decomposition in terms of temperature and reaction time, as well as the mathematical relationships represented by the yield diagrams for predicting the compositions of the products.

The yields (H_i) attained during the pyrolysis are obtained by reading, from the yield diagrams of the pyrolysis of individual hydrocarbons, the yield data corresponding to the x_j conversion of the mixture. These are multiplied by the initial molar fractions and the products are then summed up as follows:

$$H_i = \sum_{j=1}^{k} y_j H_{ji} \qquad (2)$$

Figure 2 shows a comparison of the measured yield data of the pyrolysis of the earlier mentioned six component mixture with those calculated from the yields of the individual components, under decomposition conditions of varying severity [17]. The yield data on the diagram are expressed in mole % of the starting material. A good correlation is shown on the diagram between the measured and calculated data, the deviation being less than ± 4 % (relative).

The above methods were used in calculating the yield data of gasoline fractions.

Figure 3. shows the measured and calculated yield data (in wt %) of the pyrolysis of Romashkino gasoline cuts. In the pyrolysis of gasoline cuts the aromatics in the gasoline, under the pyrolysis conditions, virtually remain unchanged and may, therefore, be considered inert. To distinguish the decomposition of the gasoline cuts containing various aromatics, the "degree of effective decomposition" was defined as the degree of decomposition of materials free from aromatics.

The diagram shows yield data corresponding to the various degrees of effective decomposition. The calculation was performed with the data of the individual hydrocarbon pyrolysis of the ten indicated components obtained under circumstances similar to those

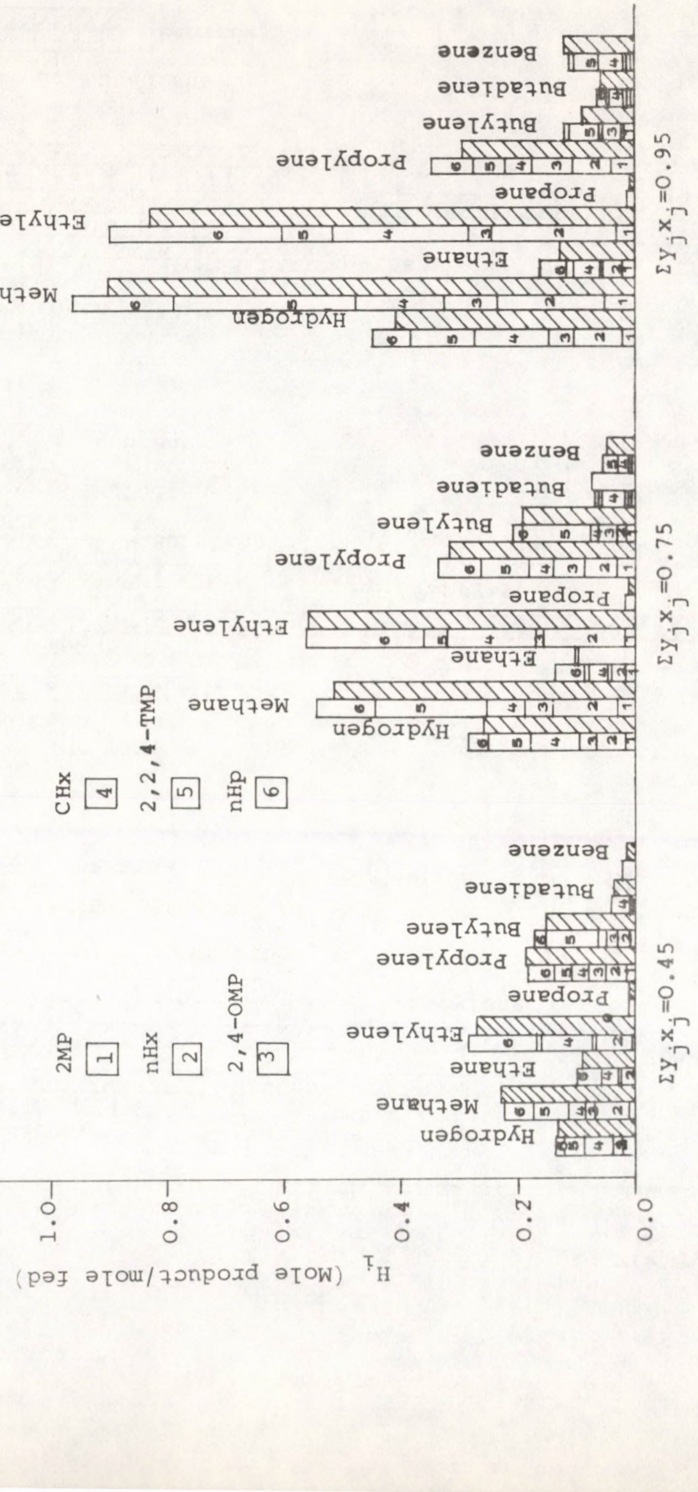

Fig.2. The measured yield data of the pyrolysis of the six component mixture and those calculated from the yield data of the individual components

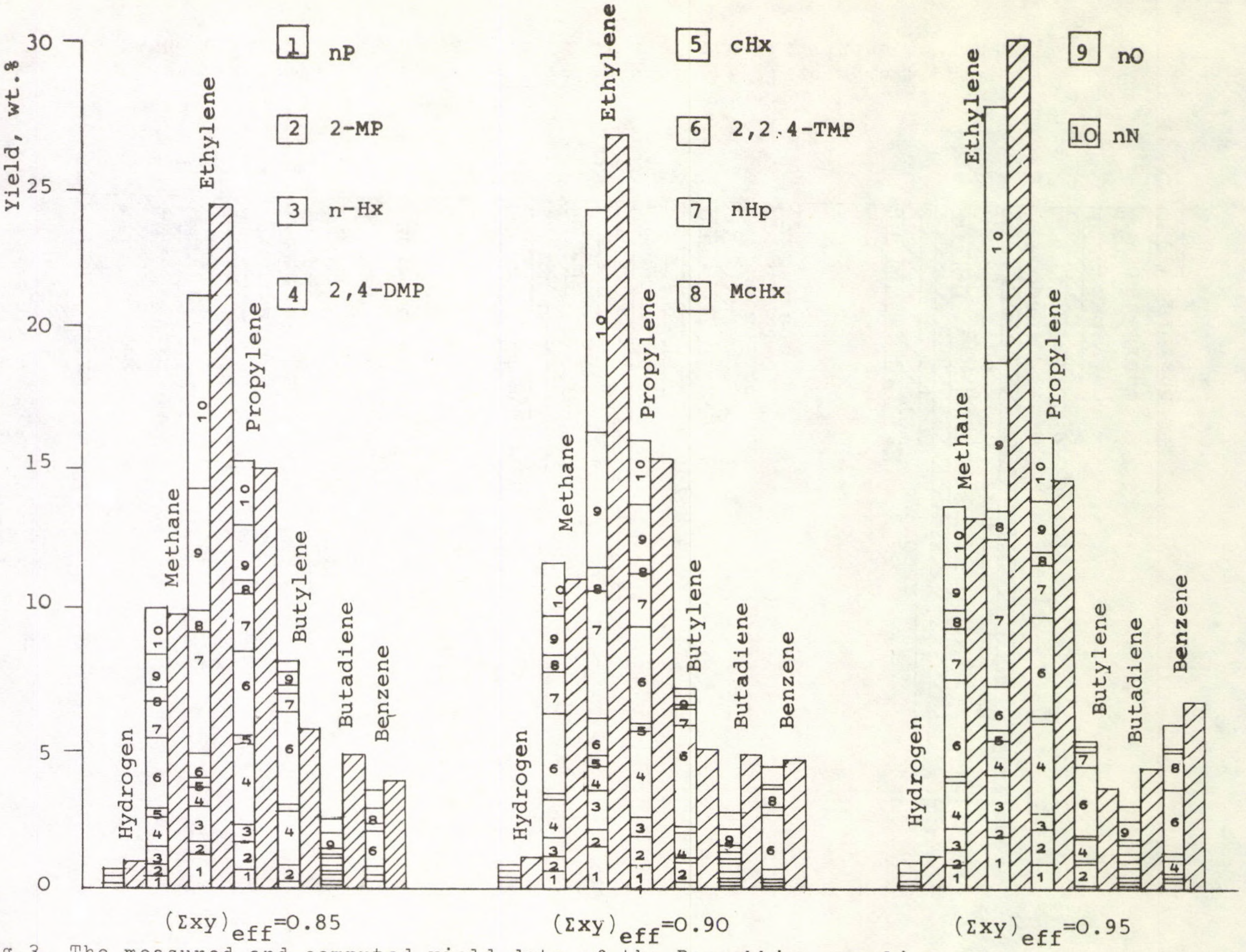

Fig.3. The measured and computed yield data of the Romashkino gasoline cut

of the pyrolysis of the six component mixture. The above mentioned ten components constituted about 70 % of the gasoline cut and the aromatic content was 8 %. As no data of more individual hydrocarbons were available for the computation, the quantity of the remaining components in the gasoline was added to that of the component whose structure it resembles most closely. This naturally reduced the accuracy of the calculations, as there existed considerable deviations among the yield data of the individual hydrocarbons. It can be seen from the diagram that despite the above mentioned approximation a sufficient correlation was obtained between the measured and calculated yield data. The deviation was, in general, 4-5 % (relative) except for ethylene where it was 10 % (relative). The higher deviation for butylene and butadiene fell practically within this range, if considered to be the sum of unsaturated C_4 hydrocarbons.

Regarding these facts, it can be established that the method used can suitable be applied in calculating the approximate yield data obtainable from the pyrolysis of gasoline cuts under varying conditions by using measured data from the pyrolysis of individual hydrocarbons found in gasoline. The method's accuracy can be improved by taking into account more of the unspecified individual hydrocarbons.

Comparison of the Results Obtained with Various Reactors

One of the important and still unsolved problems in pyrolysis research is whether the data measured in the laboratory could be used in determining the yield data and describing the operation of industrial reactors operating under considerably different conditions. On the basis of the data of pyrolysis experiments performed with Romashkino gasoline cuts in three reactors of different types and capacities as shown in Table 1., it was established that the yield data obtained with the various reactors can be correlated and evaluated in accordance with the degree of decomposition characterizing the severity of the pyrolysis.

Figure 4. shows yield curves of the main products as a function of the degree of decomposition. The curves represent the yield data measured in the laboratory isothermal isobaric reactor and in the bench-scale reactor operated under the conditions corresponding to the pressure and temperature distributions of the industrial reactor. The perpendicular lines define the deviation ranges of the measured data. The yield data, measured in the two reactors operating under considerably different conditions and represented as a function of the degree of decomposition, are within the deviation range and can be characterized by a single curve.

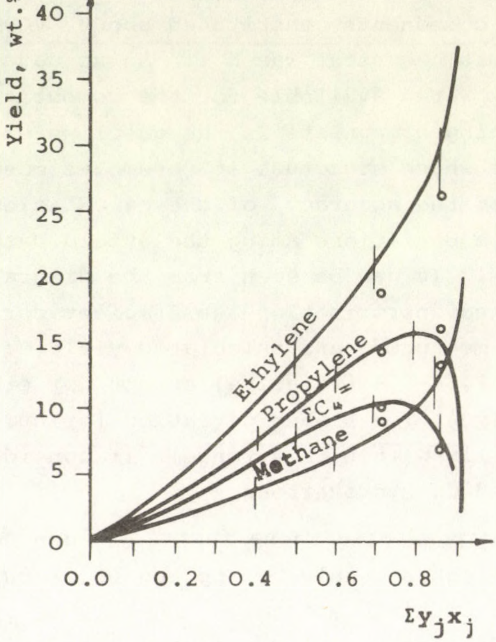

Fig.4. Comparison of yield data measured in various reactors.
— Isothermal laboratory and non-isothermal laboratory measurements
o bench-scale plant measurement

The same diagram also shows the yield data corresponding to the two different degrees of decomposition measured with a pilot plant of a capacity of 40 kg/hour of gasoline. Despite the dissimilar methods of experimentation and measurement, an acceptable agreement between the corresponding data is observed.

The Examination of the Yield Data of the Various Gasoline Cuts

In evaluating the yield data of the pyrolysis of individual hydrocarbons, it was indicated that the composition of the starting gasoline cut has a significant influence on the attainable yields. Comparative experiments were carried out with the four types of gasoline cuts (used as raw materials), under conditions similar to those in the plant in order to determine, in the bench-scale reactor, the expected product distribution of the new olefin plant.

Figure 5. shows the group composition of the starting gasoline cuts and the yield data of the main products, measured at two different values of the severity of decomposition. Although, as seen from the foregoing, the yield data may be calculated only when the individual gasoline components are known, a qualitative estimation is possible on the basis of the group composition and even the effect of the composition can be illustrated.

It is possible to compare the yields obtained for various gasoline cuts in the case of pyrolysis with severity represented by B, which corresponds to the ethylene regime.

From the diagram, it can be seen that the maximum yields of ethylene (30 wt %), propylene (17 wt %) are obtainable from the pyrolysis of light gasoline fractions and here the lowest quantity (c. 21 wt %) is that of C_{5+} liquid fraction. This is in good agreement with the conclusions drawn from the group composition distributions, i.e. the cut contains plenty of n-paraffins and isoparaffins (giving a high yield of propylene) but only 3 % of aromatics.

In terms of the yields of ethylene and propylene, the Romashkino straight gasoline cut takes second place, but both the ethylene and propylene yields are 10 % (relative) lower than the values obtained with light gasoline. Here the quantity of liquid product significantly increases, partly because of the higher boiling temperature and partly because of the higher aromatic content.

Despite its low boiling temperature, the refined gasoline is not a good basic material, because of its low n-paraffin and aromatic content. The attainable yield of ethylene is only 23.5 wt % and that of propylene is a little lower than the foregoing values. The quantity of the liquid products falls within those of the preceding cuts, but the quantities of methane and unsaturated C_4 hydrocarbons are considerably higher, especially that of isobutylene.

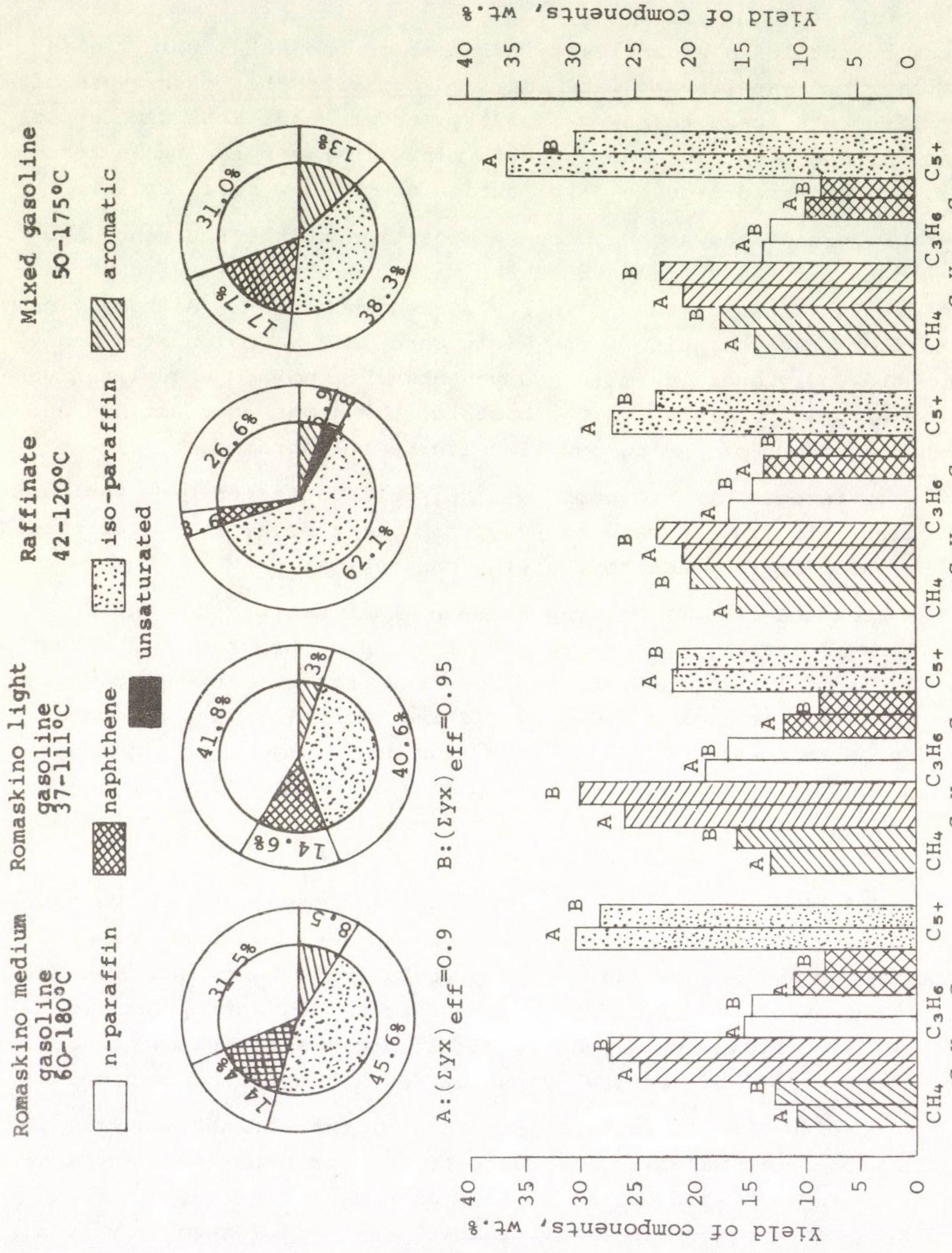

Fig.5. The effects of the quality of raw materials and operation conditions on the yields of gasoline pyrolysis products

The mixed gasoline was prepared at the Institute and met the worst permissible quality requirements for the basic material of the olefin plant. Due to its high aromatic content the ethylene yield was 23 wt %, that of propylene was about 13 wt %, but the quantity of the liquid products was the highest, being 30 wt %.

Apart from the quality of the raw material, the product distribution obtained - i.e. the yields - varied according to the conditions of pyrolysis, especially the exit temperature, the temperature distribution and the residence time.The latter conditions simultaneously determined the severity of the pyrolysis which was represented, in the foregoing discussion, as the degree of decomposition.

On the basis of the yield data at the two severities shown in Figure 5., it can be seen that by slightly varying the extent of decomposition, the product distribution was considerably modified. In the case of light gasoline cut, for example, at a degree of effective decomposition of 0.9, the yields of ethylene and methyne were lower by 13 % (relative) and 19 % (relative) respectively, whereas the respective yields of propylene and unsaturated C_4 hydrocarbons increased by 13 % and 40 % (relative) compared to the case where the degree of decomposition was B.

This meant that given the relationship between the yield data and the operation conditions, the plant could - given the raw materials or their mixture - function under conditions of optimum yields that are significant from the standpoint of application and marketing. On the basis of the results achieved so far, it was possible to take into account the effect of the quality of the gasoline cuts intended as the raw material of the olefin plant and the change in the operation conditions on the expected yields.

The aim of the present research work is the development a suitable method for the calculation and checking of the industrial pyrolysis furnaces. The next tasks can be divided into two groups:

1. The development of a method of calculating the degree of decomposition of gasoline cuts on the basis of the kinetic data of individual hydrocarbons measured in an isothermal, isobaric labo-

ratory reactor and the checking of the relationships thus obtained in a bench-scale reactor operated under industrial conditions and then with the assistance of measurements carried out with an industrial furnace.

2. The mathematical formulation of the relationships between the degree of decomposition and the operation conditions, on the basis of measurements carried out in a laboratory reactor, and then checking the results with measurements on industrial furnaces.

In the knowledge of the above mentioned data and relationships, the mathematical model of the pyrolysis furnace and its computer program can be worked out, which provide the possibility of describing the operation of industrial furnaces and computing the optimum conditions and the optimum product distribution.

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РЕЗЮМЕ

Авторами дан обзор о нескольких важных и непосредственно используемых в практике результатах пирогенетических исследований, проведенных в Венгерском Научно-Исследовательском Институте Нефти и Природного Газа. Кратко описаны аппараты и методы исследований. Представлены важнейшие результаты пиролиза отдельных углеводородов, углеводородных смесей и погонов бензина, далее показаны методы вычисления данных выхода. Сопоставлены и оценены результаты, полученные в разных реакторах. На основе опытов с разными погонами бензина показано влияние изменения качества сырья и условий процесса на достигаемый выход.

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CATALYTIC PROCESSES DEVELOPED BY MÁFKI

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A review is presented of the most important results of catalyst research and the processes developed and partially realized at plant level.

The research work involved some aspects of homogeneous and heterogeneous catalysis. An industrial process was developed for the preparation of acetone from acetylene and oxo-alcohols from cracked gasoline. Catalysts were developed for ethylene oxidation, the production and purification of synthesis gas and the oxidative removal of air-pollutants.

The Organic Chemical Department of MÁFKI - established in 1948 - developed petrochemical processes which seemed, at the initial stages of the research work, realizable at plant level under the prevailing circumstances in Hungary. In the following discussion those catalytic processes are presented, which were developed at the Department in the first few years and some of which were realized at plant level. In this report only those results and modern activities are mentioned which were achieved by MÁFKI's research teams.

1. Acetone Production

The synthesis gas obtained from the partial oxidation of methane contains 8-9 % of acetylene, which can be converted to acetone by a catalytic process. The process consists of mixing the PO exhaust gas with steam and passing the mixture through a ZnO catalyst at 350-450 °C. After the acetone thus obtained is recovered, the remaining gas contains mainly CO-H_2 synthesis gas and as impurities 0.4 % of acetylene and 5 % of methane. The impurities are burned up in a secondary oxidation and in this manner pure synthesis gas is obtained. This process was studied in detail at the Organic Chemical Department and reported in the reference literature. Figure 1. shows the flow sheet of the Laboratory Test Unit.

At the Department, intensive studies were carried out to prepare a ZnO catalyst of the required quality. The studies proved that if the catalyst contained traces of iron or heavy metal or even sulphates, then the carbon monoxide conversion was enchanced, but that a chloride content inhibited the said conversion and, therefore, favoured the desired reaction. Taking into account the above facts, a procedure was worked out by which a ZnO catalyst was obtained from solutions of Na_2CO_3 and $ZnCl_2$. On adding the solution of Na_2CO_3 to that of $ZnCl_2$ a precipitate of $ZnCO_3$ was obtained which contained few sodium, but comparatively more chloride ions. On igniting the $ZnCO_3$ at 4-500 °C, ZnO resulted whose excellent structure enhanced its catalytic properties. It was then mixed with graphite powder or dextrin and water and could be shaped into thin rods. In the course of preparing the catalyst, the use of iron vessels should be avoided, wooden or enamelled containers would suffice. By suitably purifying the product, a high-quality catalyst may be obtained even from contaminated starting materials.

Fatigue studies of the recovered catalyst were performed. We found it suitable for long lasting operation. Its fatigue time and optimal regeneration period could be expressed by an integral equation whose solution indicated an acetone production time of 200 hours and a regenation period of 29 hours. It was necessary to change the catalyst bed only after an average of nine cycles (1800 hours of operation). The catalyst fatigue appears partly in the form of a decrease in activity (conversion declines from 90 to 55 %) and partly as an increase in layer resistance. The fall in

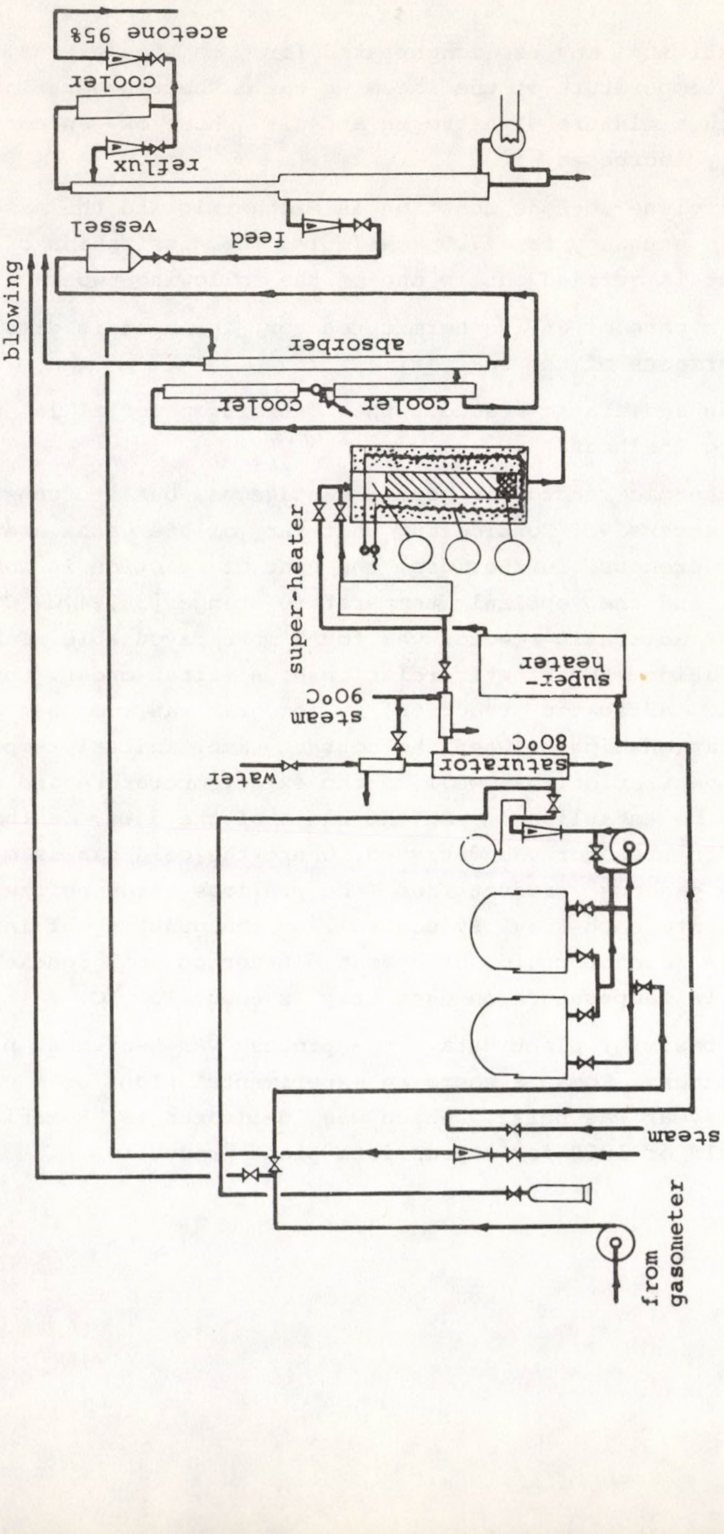


Fig.1. Flow sheet of the Laboratory Test Unit for acetylene-acetone

catalytic activity may be compensated for, to some extent, by raising the temperature of the incoming gas. The regeneration is performed with a mixture of nitrogen and air, whose oxygen content is continually increased.

The acetylene-acetone reaction is exothermic and the associated change in enthalpy is -47.0 kcal/mole. The dissipation of the liberated heat is carried out in one of the following two ways:

- in the case of an isothermic reactor, the heat is dissipated on the surfaces of the reactor,
- for an addiabatic reactor, the outgoing material is used in dissipating the heat.

The isothermic reactor is more advantageous, but its construction is more expensive. Considering that very dilute gases are involved in our process, furthermore, the heat of reaction is comparatively low and the optimal temperature range (340-440 °C) is very wide, the adiabatic reactor was found more favourable. Taking into consideration the kinetic relationships (first order, unidirectional and adiabatic reaction) a nomogram was composed from which the relationships between the contact time, initial temperature and concentration, as well as the exit temperature and conversion could be established. On the basis of the data, a three--tray adiabatic reactor was designed, where the cold gas is mixed with the hot gaseous product from the previous tray before the feed arrives onto each tray. By controlling the quantity of incoming gases the reactor could be operated under optimal conditions and the rise in temperature on each tray is about 100 °C.

On the basis of plant data, the process was tested at plant level in Buciumeni, Romania where an experimental plant of a capacity of 500 t/year was built, which was delivared to Romania in the second half of 1958 for appropriate plant production.

2. Ethylene Oxide Production

A modern petrochemical method of producing ethylene oxide is the catalytic oxidation of ethylene in the presence of a silver catalyst. In the course of our work we developed selective silver catalysts, suitable carriers, as well as a stationary and moving bed technology.

The first set of silver catalysts were prepared from silver nitrate and potassium hydroxide. The silver oxide was reduced to metallic silver in a hydrogen stream. The catalyst prepared in this way contained potassium ions and the experiments showed that a potassium content of 0.1 wt.% has an inhibitory effect. Hence, we had to use silver oxalate as the starting material which was thermally decomposed in glycol. We established that alkaline earth metals especially calcium are good prometers and stabilizers. The catalyst was prepared by precipitating the silver oxalate together with calcium oxalate and both were decomposed in glycol at 160 °C. The silver catalyst thus prepared was filtered, washed, dried and crushed. This catalyst enhances the conversion of ethylene at 200-220 °C to completion with a yield of 50-55 % of ethylene oxide and a utilization of 60 %. It was found that the promoted catalyst should be activated before use, for only in this way could the catalyst be stable.

The catalyst could best be applied in the plant tube reactor in a granulated form or on a carried. Since the catalysed oxidation, of ethylene to ethylene oxide and the following unavoidable side reactions are exothermic:

a) the total oxidation of ethylene to carbon dioxide and

b) the further oxidation of ethylene oxide to carbon dioxide,

maintaining the reaction under isothermic conditions is possible only if the heat of reaction can be dissipated by a catalyst or a carrier of high conductivity.

At first the active silver suspension was carried onto silver splinters then, after tabletting, a catalyst was obtained which, for ethylene oxide, ensured a yield of 55 % and a utilization of 45 % at 278 °C. The expensive silver carrier was replaced by aluminium. Experiments showed that metallic aluminium is not neutral to the reaction. Carriers may either be hyperactive, hypoactive or inert. The hyperactive catalysts ensure the total oxidation of ethylene to carbon dioxide at 180-200 °C, and this property is presumably the consequence of the thick oxide layer formed on the aluminium surface. The phenomena of hypoactivity, which probably arises when silver and aluminium constitute a galvanic cell in water, makes the ethylene remain unchanged in the exhaust gas. When the aluminium oxide layer is removed either chemically or mechanically from the surface of aluminium, then an inert carrier is obtained.

Catalyst soldering experiments were performed in order to establish the lifetime of the silver catalysts from which it was concluded that the catalyst prepared in the above manner could still function after 5-6,000 hours of application. The catalyst is disactivated if some hydrochloric acid comes in contact with the catalyst or if, on cutting off the supply gases, the ethylene polimerizes onto the catalyst, but such decrease in activity can be eliminated by the regeneration of the catalyst under the oxidative conditions.

To complete the technological research, the kinetics of the oxidation reactions of ethylene were also studied. To determine the reaction rate constants a computer programme was made and thus the activation energies of some of the processes were computed.

To improve the catalytic oxidation of ethylene, a reactor was developed in which the catalyst could be recirculated. The advantage of the reactor was that it permitted the occurrence of even highly exothermic reactions under isothermic conditions. By introducing gas locks into the system, it is possible to make the reacting gas flow along the required route. The catalyst column in motion was analysed according to the Ergun equation, and it was concluded that it could be treated as a stationary bed since neither the solid material nor the flow rate of the gas passing through the latter under the reaction conditions was changed. It was observed from the oxidation experiments performed in the recirculation reactor that at low temperature a very high utilization of 85-90 may be attained.

3. Catalytic Natural Gas Decomposition

The thermal decomposition of methane for the preparation of hydrogen and synthesis gas takes place chiefly catalytically. The active material in the catalyst is metallic nickel. A special catalyst was developed for the decomposition from domestic raw materials.

It was established that the optimum nickel content was 15 %.

The loadability of the catalyst, and its resistance for carbon-containing materials, etc., were determined and it was found that they agreed with those of the best imported catalysts.

4. Catalytic Air Cleaning

The organic compounds contained in air are most effectively removed by catalytic oxidation if the concentration of the material to be oxidized is below the ignition value. Various hydrocarbons can be effectively removed between 250-350 $^{\circ}$C with the help of catalysts, M-4, containing iron and manganese and developed at the Institute. The laboratory results were tested with experimental equipment with a capacity of 100 m^3/hour installed in the food industry and the plastic processing industry.

5. Low Temperature Carbon Monoxide Conversion

A study was made of the behavior of two types of catalysts composed of the alloys copper-zinc-chromium and copper-zinc-aluminium in the carbon monoxide conversion. In the course of the separation of basic carbonates, a composite crystal is formed and after reduction, copper of high activity and fine distribution is obtained. The chromium and aluminium act as stabilizers.

6. Propane Dehydrogenation

The possibility was examined of preparing propylene by dehydrogenating propane on chromium oxide - aluminium oxide catalyst both in the laboratory and at plant level.

In the laboratory, various catalysts produced in the Soviet Union, Poland and the German Democratic Republic were applied.

In the GDR, plant studies were performed at the dehydrogenating plant of the Böhlen Chemical Combine. Under the given conditions a conversion of 25-30 % and a utilization of 72-77 % were attainable.

7. Oxosynthesis

According to the classical oxosynthesis, a formyl radical may be added to the olefinic double bond in a carbon monoxide and hydrogen atmosphere and in the presence of a homogeneous cobalt catalyst. The aldehydes thus obtained are then reduced to alcohols in the presence of heterogeneous catalysts. This is the so-called two-stage technology.

To meet the demand for dioctyl phthalate plysticizers in Hungary, only thermally cracked gasoline containing olefins was available. Consequently a special oxo process had to be developed for the preparation of oxoalcohols. The major problem involved the catalytical (heterogeneous) hydrogenation of aldehydes containing sulphur compounds. As is well known, in the course of aldehyde synthesis, alcohol is formed to a small extent. This suggested the idea of developing a direct alcohol synthesis or the achievement of both stages of the process with the same homogeneous catalyst. This has many advantages over the earlier two-stage synthesis; a contact hydrogenation can be avoided and on the other hand, it is more economical, because of its simplicity.

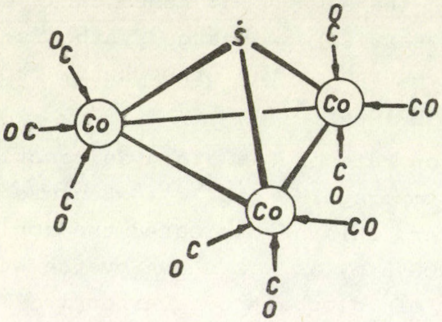
On account of the low reaction rate of the aldehyde reaction, it is advisable to apply a high temperature (210 °C). Because of carbonyl stability problems, however, this necessitated the application of CO partial pressure of 200 atm, as was shown by the studies on the equilibrium conditions of dicobalt octacarbonyl. The reaction time increases somewhat compared with that of the two-stage technology. The aldehyde reduction is, at all times, the slowest subprocess and, therefore, determines the volumetric velocity. The increased velocity is a further advantage as it permits the simultaneous transformation with a high conversion of the olefins of cracked gasoline which reacts with a different reaction rate.

From the analysis of the economic factors, it was found that the investment costs of the direct alcohol synthesis are 10 % lower than those of the classical technology. One other advantage is that because of the dilute olefins of different reaction rates, the dissipation of the heat of reaction was no problem. Hence the internal structure of the reactors is simple and inexpensive. The relatively high reaction temperature made it possible to moderate the requirements on the purity of the other raw materials.

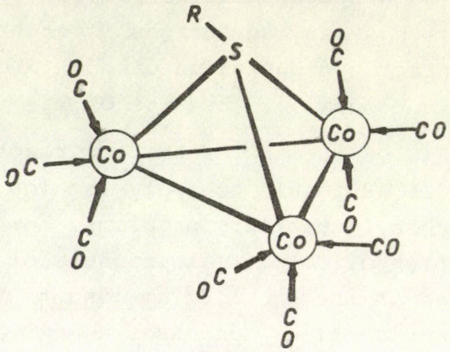
All these advantages urged the technological designing of the direct alcohol synthesis, which was realized in the form of a stationary bed, alternate reactor.

Later on, the steep rise in the sulphur content of the cracked gasoline raw material made it necessary to developed a technology using a new rotary suspension catalyst. This process permitted the processing of raw materials containing extremely large amounts of sulphur (0.1-1.0 %). At the same time, the utilization of the high pressure reaction domain increased and this improved the economic feasibility of the process.

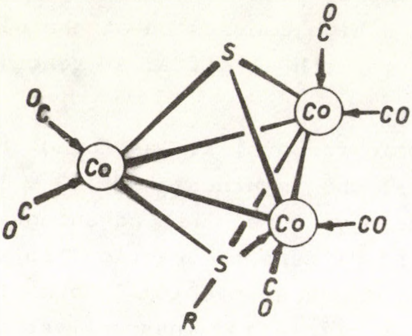
$Co_3(CO)_9S$



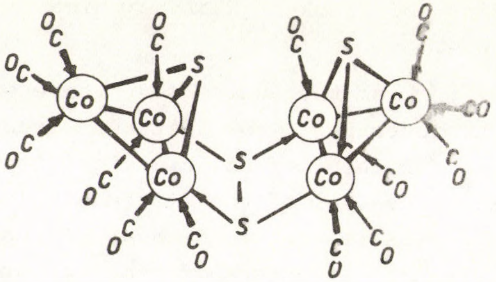
$Co_3(CO)_9(SC_6H_4CH_3)$



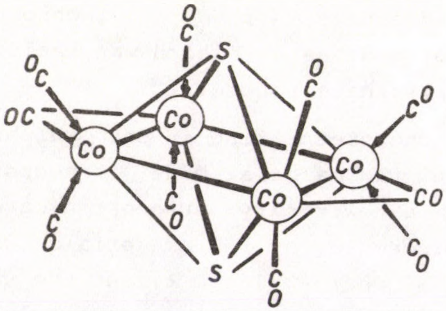
$Co_3(CO)_4(S)(SCH_2C_6H_5)$

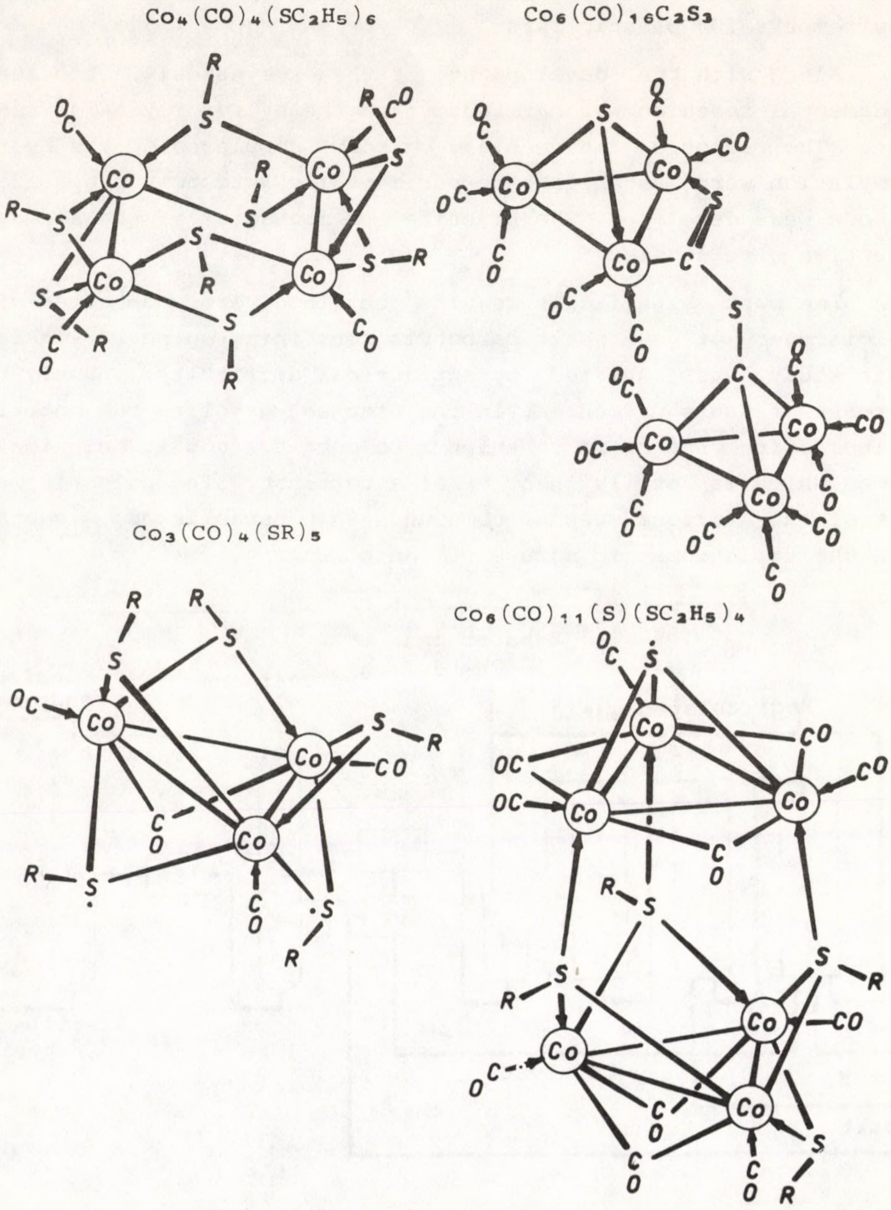


$[Co_3(CO)_7S]_2S_2$



$[Co_2(CO)_5S]_2$





$Co_4(CO)_4(SC_2H_5)_6$

$Co_6(CO)_{16}C_2S_3$

$Co_3(CO)_4(SR)_5$

$Co_6(CO)_{11}(S)(SC_2H_5)_4$

Fig.2. Cobalt carbonyl complexes containing sulphur

The manufactured product was of a quality that fulfilled the requirements for plasticizers.

Along with the development of the oxosynthesis, top level fundamental research was carried out on the hydroformylation reaction. The proposed intermediary carbonyl complexes of the hydroformylation were established experimentally and new preparatory methods were developed. The kinetics and mechanism of the aldehyde reduction were studied.

The most significant results obtained were connected with the discovery of new cobalt carbonyls containing sulphur (Figure 2). Their study was justified by a practical difficulty, namely the increase of sulphur content in the cracked gasoline raw material. By increasing the ratio of sulphur to cobalt, cobalt sulphide is formed which is totally inactive as a catalyst. The poisoning effect of the various sulphur compounds was established, together with the stoichiometric nature of the poisoning.

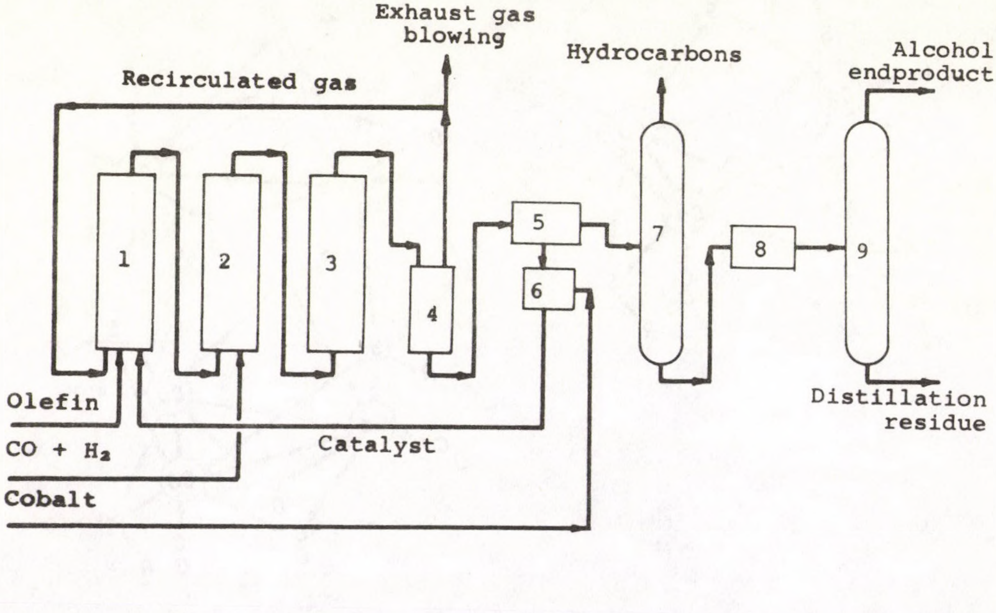


Fig.3. The flow sheet of the MÁFKI process. 1, 2, 3 - Oxoreactors; 4 - Separator; 5 - Decobalting; 6 - Catalyst regeneration; 7, 9 - Distillation columns; 8 - Ester decomposition

The direct alcohol synthesis was first applied in 1962-1964 at the Pét Nitrogen Works. Figure 3. shows the flow sheet of the process. The installation proved that by applying the homogeneous catalytic process, olefins can be transformed into alcohols with a yield of about 100 %. Later, this experimental plant had to be abandoned and no production plant was constructed, as Hungary did not possess the necessary olefin resources.

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Dr. G. Almássy, Dr. A. Balogh, Dr. J. Berty, O. Budavári, Dr. Gy. Fekete, E. Földes, F. Gersey, Dr. I. Hartwig, J. Herendi, Dr. E. Klumpp, J. Laky, O. Répásy, Á. Sárközi, Dr. E. Oltay, P. Szabó, Dr. L. Markó, Dr. I. Pallay took part in developing the catalytical processes and new catalysts.

The results obtained so far are due to their diligent and conscientious work.

РЕЗЮМЕ

Автором дан обзор о важнейших результатах исследований катализаторов проведенных от самого начала существования института, а также о разработанных процессах, частично внедренных уже в производство.

Работы распространялись на разные области гомогенного и гетерогенного катализа; был разработан способ получения ацетона (из ацетилена) и оксоспиртов (из пирогенного бензина) в производственном масштабе. Были созданы катализаторы для окисления этилена, производства и очистки газов синтеза и удаления загрязнений воздуха окислением.

Tájékoztató a közlemények szerzői részére

1. A „Hungarian Industrial Chemistry" a veszprémi vegyipari tudományos intézmények közös kiadványa, amely angol, orosz, francia vagy német nyelven írt, a vegyipart közvetlenül érintő alkalmazott és alapkutatások eredményeivel, a vegyipari folyamat-, eljárás- vagy műveletttannal foglalkozó eredeti közleményeket tartalmaz. A szerkesztőbizottság a veszprémi intézmények alkalmazottain kívül azok részére is lehetővé teszi eredményeik közlését, akik a megjelölt tudományterületen dolgoznak, és a megjelenő kémiai tárgyú folyóirataink adott profilja miatt nincs megfelelő lehetőségük munkáik hazai publikálására.

2. A magyar nyelven írt kéziratok a főszerkesztő címére (*dr. Bodor Endre*, Veszprémi Vegyipari Egyetem, Veszprém, Schönherc Z. u. 10.) közvetlenül küldhetik a szerzők rövid levél kíséretében.

3. A kísérőlevélben a szerző(k)nek nyilatkozni kell arról, hogy

a) a beküldött kézirat önálló munka, a közölt eredmények ebben a formában más tudományos folyóiratban nem kerülnek publikálásra;

b) a fenti négy nyelv közül melyiken kívánják a közlést;

c) a cikk elfogadása után saját maguk kívánják-e a fordítást elvégezni vagy a szerkesztőség gondoskodjék-e a fordításról;

d) ill. közölniük kell a cikk szerzőjének — több szerző esetén annak az egy szerzőnek — a nevét, pontos címét és telefonszámát, akivel a szerkesztőség a nyomdai munkák elvégzése idején a kapcsolatot felveheti.

A kísérőlevelet a kutatóintézet, tanszék vagy üzem vezetőjének a közlést engedélyező láttamozásával kell ellátni.

4. Az A/4 formátumú papírra írt, első példányú kézirat első oldalára csak a közlemény címét, a szerző(k) nevét és munkahelyét, valamint a munka maximálisan 15 sor (soronként 50 leütéssel) terjedelmű összefoglalóját kérjük gépeltetni. A táblázatok a szöveg közé gépelendők, az irodalom felsorolása, az ábrák és az ábraaláírások a kézirat végére kerüljenek. A lábjegyzeteket az illető lap aljára gépeljük. Lehetőleg az ábrák se legyenek A/4 méretűnél nagyobbak.

Kérjük a szerzőket, hogy cikkeikben lehetőség szerint a „*John H. Perry:* Vegyészmérnökök kézikönyve I.—II. kötet, Műszaki Kiadó, Budapest, 1968-1969" c. műben szereplő mértékegységrendszert és jelöléseket alkalmazzák. Ugyancsak kérjük azt is, hogy a magyar nyelvű kéziratokat a „Magyar kémiai elnevezés és helyesírás szabályai I.—II. kötet, Akadémia Kiadó, Budapest, 1972" figyelembevételével írják meg.

5. A szerzőket szerzői díj és összesen 50 db. különlenyomat illeti meg. A különlenyomatok önköltségi árát a szerzői díjból le kell vonnunk. Amennyiben a fordítást is a szerző végzi, a fordítói díjat is átutaljuk részére.

A kiadásért felelős: Dr. Nemecz Ernő
Felelős szerkesztő: Dr. Bodor Endre
Példányszám: 950 + 250 különlenyomat cikkenként
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Veszprém (Hungary)

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СОДЕРЖАНИЕ

PREFACE

In 1974, the Research Institute for Heavy Chemical Industries (NEVIKI) celebrated the twenty fifth anniversary of its foundation. The scientists of the Institute succesfully worked in the fields of the production and application of pesticides, inorganic chemical technology, corrosion, unit operation and process control, air pollution and radiochemistry and such scientific research work was extremely valuable for the Hungarian chemical industry. More than one thousand original papers were published during these twenty five years, which were mainly printed in the Institute's own periodical.

On the occasion of the anniversary and to represent the scientific research work carried out in the Institute, twenty one papers were presented in the fifth volume of the "Nehézvegyipari Kutató Intézet Közleményei", and eight articles were published in the twenty ninth volume (No.8) of the "Magyar Kémikusok Lapja". A scientific session was also organized during the Jubilee, and some of the lectures that were delivered are collected and published here.

Dr. András Szántó

General Manager

ПРЕДИСЛОВИЕ

Исследовательский Институт Основной Химической Промышленности торжествовал 25-летнюю годовщину его существования. Сотрудники Института выполняют успешную научно-исследовательскую работу, значительную и полезную для химической промышленности Венгрии, в областях химии и применения средств для защиты растений, технологии по неорганической химии, коррозии, техники процессов и управления, защиты окружающей среды и радиохимии. Результаты работ прошлых 25 лет были опубликованы в 1039 сообщениях , значительная часть которых появилась в самостоятельном журнале Института.

С целью ознакомления читателей с научными исследованиями, проводящимися в Институте, к случаю юбилея были опубликованы в Журнале Исследовательского Института Основной Химической Промышленности, в томе 5, всего 21 сообщений, а в Журнале Венгерских Химиков, в номере 8 тома 29 всего 8 сообщений. К случаю юбилейных торжественных событий была организована научная сессия, из докладов которой выбрано опубликуемое здесь несколько сообщений.

Др. А. Санто
директор

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PREPARATION AND EXAMINATION OF A NEW, HIGHLY POTENT LARVICIDE

B. NAGY, M. NÁDASY and I. KECSKEMÉTI*

(Research Institute for Heavy Chemical Industries, Veszprém
*Public Health Institution, Veszprém Country)

The production technology of Nephis 1 G was developed; in the course of biological tests it presented an excellent larvicide action.

The active ingredient of the larvicide is 0,0,0',0'-tetramethyl-(0,0'-thiodi-p-phenylene)-thiophosphate, first produced in the laboratory of the American Cyanamide Co. By the application of the technology developed in the course of the present work, the product can be produced with a simple and economic process with a yield of 75-80 % at a purity of 90 %.

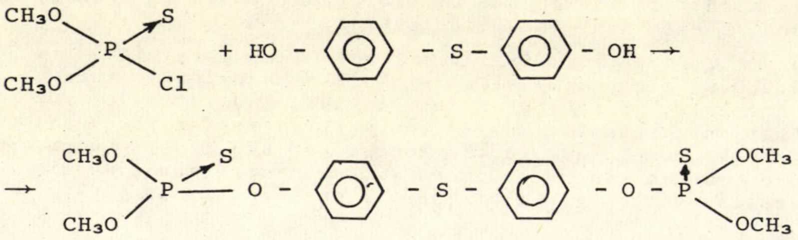
Introduction

A recurring assignment of Hungarian public health every year is the struggle against mosquitoes in various recreation areas. There are two possibilities of organized defence: first, the treatment of the area to be protected with a suitable pesticide by spraying or powder sprying, or by destruction of the mosquito larvea at the breeding place. The latter method is considerably cheaper, considering that a breeding place representing as little as a few square metres can produce hundreds of thousands of mosquitoes. So far application of this method has been very difficult, because the larvicides known up to the present time had a very high toxicity against fishes. However, a technology developed in the Research Institute for Heavy Chemical Industries enabled the preparation of a mosquito larvicide - Nephis 1 G - which overcomes this drawback.

The new procedure is described in the following:

Description of the Experiments

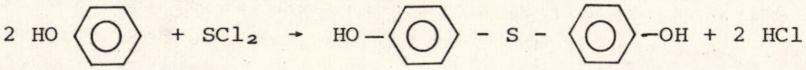
The active ingredient of Nephis 1 G is O,O,O',O'-tetramethyl-(O,O'-thiodi-p-phenylene)-thiophosphate, which can be prepared in the following manner:



In the course of the experiments 4,4'-dihydroxi-diphenyl sulphide was prepared first, and thereupon O,O-dimethyl-chloro-thiophosphate, and finally Nephis were prepared.

Preparation of 4,4'-dihydroxi-diphenyl sulphide

The procedure was developed on the basis of a reaction known from literature. The reaction can be described by the following Equation [2]:



In a three-necked spherical flask, equipped with a stirrer, thermometer, feeding funnel, condenser and a hydrochloric acid scrubber, 2 moles of phenol and 2 litres of carbon tetrachloride were weighed in. One mole of sulphur dichloride was dropped into the solution at room temperature in a period of about 1 hour. The product separated in the form of yellowish-white crystals which can be recrystallized from benzene. The action of the following parameters was studied in these experiments:

temperature of reaction
time of reaction
mole ratio
rate of stirring

On the basis of these experiments, the optimum parameters of the preparation of 4,4'-dihydroxi-diphenyl sulphide are the following:

Materials fed in:

phenol		1 mole
SCl_2		0.48 mole
CCl_4		1000 ml
benzene		1500 ml
temperature		5-10 ^oC
reaction time		1 + 2 hours
rate of stirring		800 r.p.m.
yield of product		65 %
purity	minimum	95 %
melting point		150-152 ^oC

On the basis of the aforesaid, the optimum laboratory procedure for the preparation of 4,4'-dihydroxi-diphenyl sulphide is the following:

1 mole of phenol and 1000 ml of carbon tetrachloride are weighed into a flask equipped with a stirrer, thermometer, dropping funnel, condenser and hydrochloric acid absorber. The mixture is

cooled to 5 °C and the addition of 0.48 mole of SCl_2 is started; the addition is made dropwise during one hour. Hereupon the mixture is stirred at 20 °C for two hours and the precipitate separated is filtered, dissolved in 1500 ml of hot benzene and cooled. The weight of the precipitate separated is 75 g, its melting point is 151 °C. The yield is 65.8 %.

Preparation of O,O-dimethyl chlorothiophosphate

O,O-dimethyl chlorothiophosphate was prepared according to a procedure developed in our Institute in 1967 [1].

In a spherical flask of 3 litres capacity, equipped with a stirrer, thermometer and dropping funnel, 960 g (30 moles) of methyl alcohol are added at a uniform rate to 1965 g (10 moles) of phosphor thiotrichloride with vigorous stirring and cooling at 5-10°C within a period of two hours. The whole mixture is poured into a separating funnel and the lower, organic physe is separated from the aqueous phase, and repeatedly washed with 500 ml of water. After separation, the organic phase is brought back into the flask, cooled to 5 °C and 960 g (30 moles) of methyl alcohol are added at such a rate that the temperature of the mixture should not get higher than 10 °C. Hereupon 1100 g of 40 % aqueous sodium hydroxide solution is added with vigorous stirring and cooling at 5-10 °C. After the addition, the mixture is stirred without further cooling for a period of one hour. After the reaction, the salt is dissolved from the product with 2500 ml water and after sedimentation technical dimethyl chlorothiophosphate is obtained as the lower phase.

Preparation of Nephis

The active ingredient can be prepared in the following manner: 4,4'-dihydroxi diphenyl sulphide is dissolved in 10 % NaOH solution and the addition of dimethyl chlorothiophosphate is started.

After continued stirring the organic phase is separated, washed with water and alkali, and the traces of water are removed by distillation and the product is obtained as the residue. The reaction is exothermic to a small degree, however, the amount of heat produced is low so as not to make cooling necessary in practice. Taking this fact into consideration it is preferable to start the addition at 40 °C and carry it out in such a manner that at the end of the addition the temperature of the reaction mixture is in the vicinity of 60-70 °C and final stirring is carried out at that temperature.

In the course of the systematic experiments, the effect of the following parameters was studied in detail:

purity of the starting materials
temperature
reaction time
mole ratio

The Optimum Laboratory Procedure for the Preparation of Nephis

120 g (0.55 mole) of 4,4'-dihydroxi diphenyl sulphide is weighed into a 1-litre spherical flask equipped with a stirrer, thermometer, feeding funnel and reflux condenser and 440 ml (1.1 moles) of 10 % sodium hydroxide solution is added. The addition of 160 g (1 mole) dimethyl chloro thiophosphate is started at 40 °C and the addition is carried out during a period of half an hour.

During the addition, the temperature reaches 60-70 °C and the mixture is stirred at that temperature for three hours. The organic phase produced is separated after cooling and washed with 2x200 ml portions of water, 2x100 ml portions of 10 % Na_2CO_3 solution and 2x100 ml portions of water.

After separation, traces of water are removed by distillation in a vacuum, and the product, a light brown oily liquid is obtained as a distillation residue. The weight of the material is 220 g, 0.47 mole. Its refractive index at 20 °C is 1.5865.

Its purity is minimum 85 %.

On the basis of the aforesaid, the characteristic parameters of the procedure developed for the preparation of Nephis are the following:

Material fed in	Amount, moles	Purity %
4,4'-dihydroxi diphenyl sulphide	1.1	95-99
NaOH	1.1	minimum 99
water	22	
dimethyl chlorothiophosphate	1.0	minimum 95
Na_2CO_3 used for washing	0.18	
water used for washing	44	
yield of technical product, as referred to dimethyl chloro thiophosphate		85-90
purity of the technical product		minimum 90
yield as referred to the pure product		75-80
n_d^{20}		1.5860-1.5880
d_4^{20}		1.300-1.320

Application of the Active Ingredient

The active material was applied in the form of a 1 % granulate. A 50 % acetone solution was prepared of the technical-grade active ingredient and the solution was sprayed upon sand obtained from the Fehérvárcsurgó sand-pit by means of a spray-gun in such a manner that the sand was mixed in a drum of 45° tilting angle and the acetone solution was sprayed upon the sand. The acetone evaporated quickly and the active ingredient remained on the sand.250 g of the active material was dissolved in 300 ml of acetone and the solution was sprayed on 25 kg of sand.

The grain size distribution of the sand was the following:

below 0.1 mm	5.6 %
0.1 - 0.25 mm	63.6 %
0.25 - 0.5 mm	25.2 %
0.5 - 1.0 mm	5.6 %
above 1 mm	0

In practice, this granulate proved to be very good and it gave a result that was similar to that of the American preparation: Abate IG.

Biological Examination

In the course of the experiments the material was applied for the treatment of mosquito larvae breeding places whose water was not in direct contact with that of Lake Balaton. The experiments were carried out in the Balatonalmádi and Balatonfüred areas and in the course of these, Abate IG a product of the American Cyanamide Co. was compared to Nephis IG.

The time and the results of the breeding places are presented in Table 1 (Balatonfüred) and Table 2 (Balatonalmádi). As it is apparent from the data presented in the Table, no difference in the permanence of the two products was observed. Instant larvicide action is reliable in the case of both preparations; the larvae are killed within 24 hours. However, the permanence of the action is in the case of both preparations as low 3-4 weeks, despite the very high doses used in these experiments. This statement is not contradicted by the fact that in the breeding places Balatonalmádi No. 6 and No. 7 an action extending for the whole summer could be

Table 1. Balatonfüred: Experiments in various seasons

No. of breeding place	June			July					August				September				
	10-	17-	24-	1-	8-	15-	22-	29-	5-	12-	19-	26-	2-	9-	16-	23-	30-
1.	+	+	+	+	+	⁝+⁝	-	-	⁝+⁝	-	⁝+⁝	-	-	0	0	0	0
2.	⁝+⁝	-	-	-	0	0	0	0	⁝+⁝	-	-	0	0	⁝+⁝	-	0	0
3.	⁝+⁝	-	-	-	+	⁝+⁝	-	-	⁝+⁝	-	-	0	0	⁝+⁝	-		
4.	+	⁝+⁝	-	-	-	⁝+⁝	-	-	⁝+⁝	-	⁝+⁝	-	-	-	+		
5.	+	⁝+⁝	-	0	0	0	0	0	⁝+⁝	-	0	0	0	0	0	0	0
6.	+	+	+	+	+	⁝+⁝	-	-	⁝+⁝	-	⁝+⁝	-	-	+	-	-	-
7.	+	⁝+⁝	-	0	0	0	0	0	⁝+⁝	0	0	0	0	0	0	0	0

Legend: + breeding; - no breeding; 0 dried up; ⁝⁝⁝ killing of larvae

Table 2. Balatonalmádi: Experiments in various seasons

No. of breeding place	June			July					August				September		
	10	17-	24-	7	8-	15-	22-	29-	5-	12-	19-	26-	2-	9-	16-
1.	+	+	⁙+	-	-	-	+	⁙+	-	-	⁙+	-	-	-	-
2.	+	+	⁙+	-	-	-	+	⁙+	-	-	⁙+	-	-	-	Ø
3.	+	+	⁙+	-	-	-	+	⁙+	-	-	Ø	Ø	Ø	Ø	Ø
4.	+	+	⁙+	-	-	-	+	⁙+	-	-	⁙+	-	-	-	-
5.	+	+	⁙+	-	-	Ø	Ø	Ø	Ø	Ø	Ø	Ø	Ø	Ø	Ø
6.	+	+	⁙+	-	-	-	-	⁙+	-	-	⁙+	-	-	-	Ø
7.			⁙+					⁙-			⁙-				

Legend: + breeding; - no breeding; Ø dried up; ⁙ killing of larvae observed. The explanation for the relatively short permanence of action (as opposed to data found in literature) may be found in the fact that in all of the breeding places, which did not get dry within 2-3 weeks, a careful study, carried out afterwards, revealed in all cases a slow streaming of the water.

Accordingly, the permanence of the action was not limited by the decomposition rate of the active ingredient, but by the rate of dissolution from the carrier material. Considering, however, the fact that on the shore of the Lake Balaton, and probably in the whole country, the character of permanent mosquito breeding places is similar to that mentioned in the foregoing, it is to be expected that the permanence of the treatment is not longer than 3-4 weeks.

Prior to treatment of the breeding places, mosquito larvae were collected for the purpose of identification. The result of these examinations is the following:

Balatonfüred:	number
Culex pipiens pipiens l.	1,058
Culex pipiens molestus Fork.	16
Theobaldia annulata Achr.	60
Aedes caspius Pall.	22
Anopheles bifurcatus Meig.	3
Unidentified young specimens	68

Balatonalmádi:	number
Culex pipiens l.	93
Anopheles bifurcatus l.	14
Theobaldia annulata Schr.	37
Unidentified young specimens	16

The genus spectrum of the larvae collected from the breeding places convincingly showed that the treatment was also successful from the point of view that the imagoes of the killed genuses of larvae later made only a negligible fraction of the detected harmful mosquitoes.

The results of the determinations carried out on the larvae also showed that finding and treatment of the breeding place has to be done beginning in March in order to be able to find and kill the larvae of Aedes annulipes and Aedes vexans, representing a considerable proportion of all genuses.Unfortunately, the breeding place of the most important genus of mosquitoes: Taeniorhynchus (Mansonia) richardii Fic. is the Scirpeto-Phragmitetum on the shoreline, which - due to its direct contact whith Lake Balaton - was not treated in this year.

As it is apparent from the experiments carried out with the larvicides, larvae can safely be killed by Abate and Nephis. However, the condition of success is that the treatment should be carried out at the appropriate time, because the pupas are practically insensitive against Abate. No adverse action upon the fauna could be observed despite the very high doses used; accordingly, with the lower doses to be used in later work, no harm is expected.

Evaluation

It was concluded that the active material produced in these experiments was identical to that produced abroad.

Experiments carried out with large doses of Abate and Nephis granulates in order to kill mosquito larvae showed the following:

a) Both preparations reliably kill mosquito larvae, but are ineffective against pupas;

b) Examination of the breeding places treated in these experiments showed that the time of action was 3-4 weeks in the case of both materials without any adverse action upon the fauna.

REFERENCE

1. NEVIKI-report 170, 1967, Veszprém

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РЕЗЮМЕ

Авторами разработана технология производства средства "Nephis 1G" проявляющего при биологическом испытании отличное инсектицидное действие против личинки комаров. Действующим началом средства является O,O,O',O'-тетраметил-(o,o'-тиоди-п-фенилен)-тиофосфат, полученный первый раз в лаборатории "American Cyanamid Co.". Согласно технологии, разработанной авторами, можно получить продукт путем простого и экономичного процесса при выходе 75-80 % и в чистоте около 90 %.

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PREPARATION OF ACID ANILIDE-TYPE HERBICIDES AND THEIR TESTING IN A FEW CULTURE PLANTS

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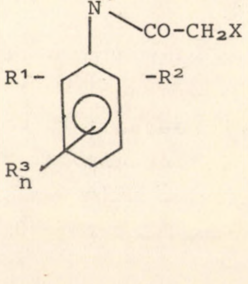
Procedures were developed for the preparation of alachlor [2-chloro-2',6'-diethyl-N-(methoximethyl)-acetanilide], butachlor [2-chloro-2',6'-diethyl-N-(butoximethyl)-acetanilide] and azetochlor [2-chloro-2'-methyl-6'-ethyl-N-(ethoximethyl)-acetanilide].

A product containing 60 % active ingredient was prepared from the latter (NEVIREX 60 EC) and it was tested on the test plots of the Research Institute for Heavy Chemical Industries (NEVIKI), simultaneously comparing it with a number of triazine and urea derivatives. NEVIREX 60 EC was more effective than all of the other preparations, without causing any damage in culture plants.

Acide anilide-type herbicides were first introduced by the Monsanto company in 1968. The considerable interest in these products was due to their excellent effect and to the fact that no phytotoxic effect could be observed on culture plants.

The active ingredients of the acid anilide type herbicides can be described by the following general formula:



R^1 = C_{1-10} alkyl
R^2 = H; C_{1-8} alkyl; C_{1-4} alkoxy
R^3 = H; C_{1-8} alkyl; C_{1-4} alkoxy; halogen
R^4 = H; C_{1-18} alkyl; alkenyl, alkynyl
x^1 = halogen; C_{1-4} alkoxy
x = halogen
n = 0 - 3

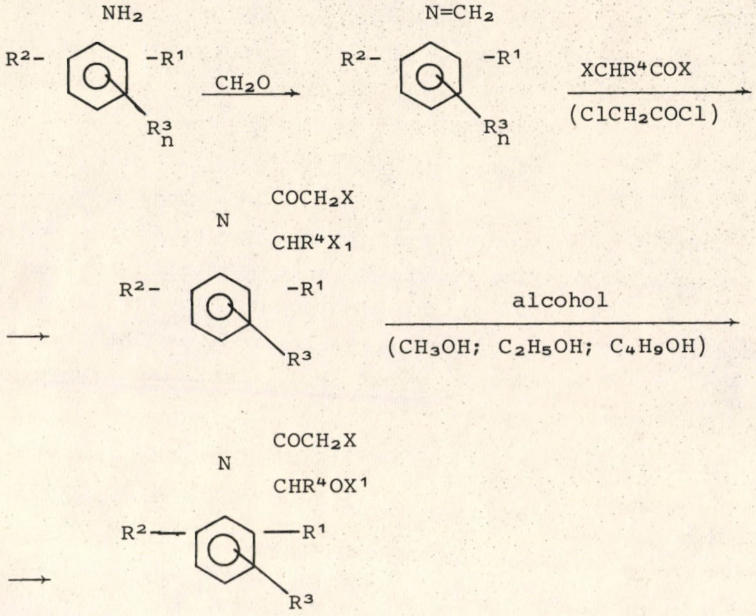
Relatively few papers dealing with the preparation of the above mentioned compounds could be found in literature.

The first step of the manufacturing technology is the preparation of the corresponding alkylated aniline derivative [1, 2]; catalytic alkylation is the most preferable way to carry out the aromatic amine-olefine reaction. The simplest catalyst is aluminium, which is soluble in the amines. Dissolution can be promoted by treatment with $HgCl_2$. Activity enhancing materials are also known, such as the metal halides of the VIII/b column of the Periodic System.

The ortho-orientation is explained by the electron deficiency of the aluminium present in the anilide [2]. The unsaturated bond of the olefine becomes polarized and the π electron pair saturates the electron orbit of aluminium. One carbon atom of the olefine becomes positively charged and probably becomes oriented towards the ortho-carbon atom of the aniline having a weak negative charge, whereby a cyclic compound is temporarily formed. Finally, transition of the proton to the olefine brings about a real bond and the connection to the aluminium is terminated. Formation of the ring may be hindered by steric factors. Such an effect is encountered in the alkylation of N-alkyl-anilines, where an alkyl group can enter the ring at only one point.

The reaction occurs at a high temperature - over 300 °C- and at a high pressure. It was concluded in the course of the experiments that the time of the reaction is considerably decreased by increasing the pressure, in the case of a catalyst concentration of 5 mole %. The crude alkylated amine was purified by vacuum distillation on a column corresponding to 6-8 theoretical plates.

Acid anilide can be produced from the substituted aniline, prepared according to the foregoing, in accordance with the following reaction:



This series of reactions is protected by a patent owned by the Monsanto company [3-4].

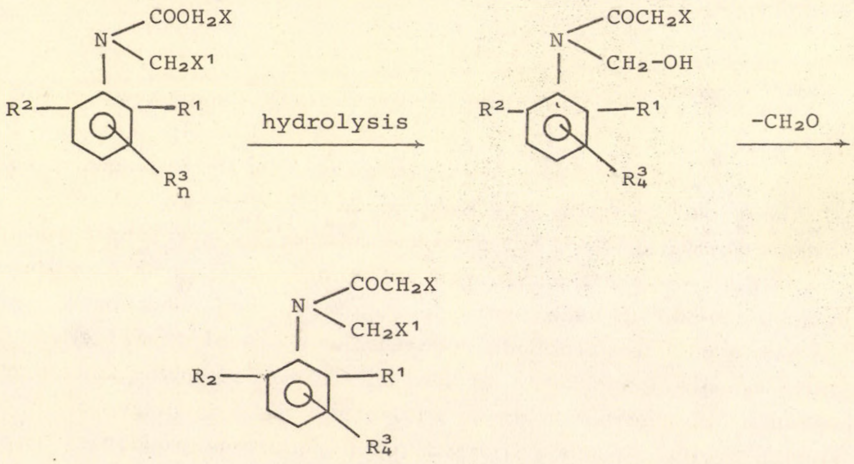
The first step is the preparation of the N-methylene derivative. The aromatic amine is made to react with formaldehyde and the water formed is removed from the system by azeotropic distillation. Inert organic solvents can be used in the experiments (such as benzene, toluene, xylene, n-hexane, and n-heptane).

Solide paraformaldehyde, containing 78 % of formaldehyde, was applied - in an excess of 30 % - as a formaldehyde Source.The temperature of the solution is preferably raised only to that of the distillation, since polymerization reactions occur at higher temperatures and the material is transformed to a highly viscous, black product. The polymerization is highly exothermic. Water has to be removed quantitatively by distillation, because it interferes with the subsequent reaction to a high degree.

The mixture was cooled and made to react with halo-acetyl halide in the presence of solvent, and the corresponding N-(halo-methyl)-acetanilide was thus formed. The reaction occurs momentarily and is strongly exothermic. It is preferable to choose the solvent, so as to be able to use the same solvent in all phases of the series of reactions.

As the last step of the reaction, the corresponding ether derivative was prepared. The reaction can be carried out in the presence of alcohol and an acid binding agent. Formation of the alcoholate occurs with a satisfactory yield only in the presence of a large - fivefold - excess of alcohol and in an anhydrous medium. Triethyl amine was applied as the acid-binding agent.

The series of reactions can be carried out with a brutto yield of 80—85 % and the purity of the product is as high as 90—95 %. The corresponding ω-chloro acetanilide is formed as a by-product, in the following reaction:



Hydrolysis occurs upon the effect of the water present, and consequently it is important in the preparation of azomethine to remove all of the water from the system by distillation.

An emulsifiable concentrate of 60 % active ingredient content was made from the azetochlor. The NEVIREX 60 EC herbicide was tested on the test plots of NEVIKI. The product was applied in a dose of 1-8 kg/ha as a pre-emergence herbicide and it was compared with a number of "Urea, Patorane, Malorane and Triazine (Hungazin PK) derivatives. The tests gave the following results (Table 1).

Table 1. Effect of the herbicide NEVIREX on maize and potato, as compared with a few licensed product

Product	Dose	Weed coverage of the culture, %	
		potato[1]	maize[2]
NEVIREX	2 kg/ha	18	3.5
	4 kg/ha	10	1.0
	8 kg/ha	4	0.3
Control		70	25.0
Patoran	4 kg/ha	38	-
Maloran	4 kg/ha	40	-
Hungazin PK	3 kg/ha	-	4.0

- = no data available

[1] Sprayed on May 11, last evaluation on August 16.

[2] Sprayed on May 24, evaluated on July 9. Maize treated with NEVIREX was still weed-free on August 19.

As a concise summary it can be concluded that the selectivity of NEVIREX 60 EC is excellent, it caused no damage to the culture even at a dose as high as 8 kg/ha, whereas urea derivatives damage potato in such a dose.

Promising experiments were also carried out wich soybeans however, as a result of climatic damage, no final evaluation could be made.

It was concluded in the course of the present experiments that NEVIREX 60 EC, applied in a dose of 2-3 kg/ha, is superior to all the products acting in one season and phytotoxic symptoms could not be observed in culture plants.

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РЕЗЮМЕ

Авторами был разработан процесс получения алахлора [2-хлор-2',6'-диэтил-N-(метокси-метил)-ацетанилид], бутахлора [2-хлор-2',6'-диэтил-N-(бутоксиметил)-ацетанилид] и ацетохлора [2-хлор-2'-метил-6'-этил-N-(этоксиметил)-ацетанилид].

Из последнего было приготовлено средство содержащее 60 % действующего начала (NEVIREX 60 EC) и было опробовано на опытных полях Исследовательского Института Основной Химической Промышленности, сравняв его с несколькими производными триазина и мочевины. Средство NEVIREX 60EC превышало действие всех остальных препаратов, при этом не нанося ущерб культурным растениям.

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PREPARATION OF THE ACTIVE INGREDIENT "GARDONA" AND ITS INTERMEDIATE PRODUCT AT PILOT-PLANT SCALE

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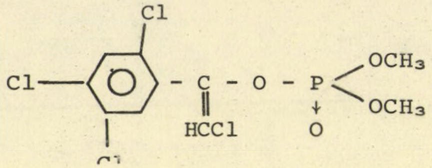
The active ingredient of the "Gardona" trade marked pesticide is " tetrachlorvinphos preparation of the latter was studied at a laboratory and, later, at a pilot plant scale in the last few years. The production of this preparation in Hungary was deemed preferable due to its advantageous spectrum of action - as apparent from data published in literature - its very low toxicity towards warm blooded creatures and seemingly simple preparation.

In the course of these investigations, the optimum parameters of the Friedel-Crafts reaction of 1,2,4-trichloro benzene and dichloro-acetyl chloride were determined. The pentachloro-acetophenone obtained was dried by azeotropic distillation and the condensation was carried out with trimethyl phosphite in light petrol. The raw technical active ingredient was separated from the petrol solution by cooling; after washing and drying it can be formulated.

"Gardona" is a pesticide introduced by Shell [1] in 1966. It aroused considerable interest, which can be accounted for by its excellent selective insecticide action and its low toxicity towards mammals. The chemical denomination of the active ingredient is cis-2-chloro-1-(2,4,5- trichlorophenyl)-vinyl-dimethyl phosphate, the common name of the compound being tetrachlorvinphos. The technical product of 98 % purity is a white, crystalline product of a melting point of 95–97 °C [2].



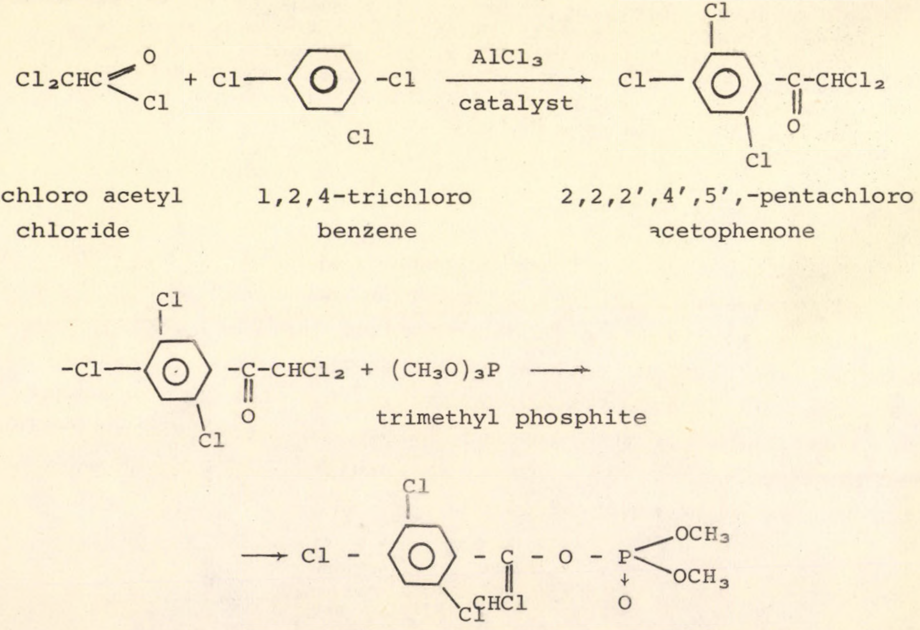
It is hydrolysed rapidly in an alkaline and slowly in a neutral or acidic medium.

Its toxicological data are the following; acute oral LD_{50} on a male rat: 1500—5000 mg active ingredient/body weight kg; on a mouse: 5000.

Acute dermal LD_{50} on a rabbit: 2500.

The active ingredient can very well be used against various fruit tortricidae moths and flies; it can also be used shortly before harvest [3].

On the basis of the favourable information mentioned in the active ingredient within the countary was considered. The chemical processes to be carried out are illustrated by the following reaction symbols:



According to the example presented in the patent [1], the procedure is the following: 99 g of anhydrous aluminium chloride is added to 109 g 1,2,4-trichloro benzene and 88 g of dichloro acetyl chloride is added dropwise to the slurry, formed by the first two compounds, within a period of 10 minutes. The mixture is slowly heated to 90 °C and kept at that temperature for a period of 4 hours. The aluminium chloride complex formed is poured on a mixture of ice and hydrochloric acid, extracted with ether, washed and eventually distilled. In this manner, 134 g of 2,2,2′,4′,5′-pentachloro acetophenone was obtained, whose boiling point at a pressure of 0.05 Torr was 103–105 °C.

The above distilled product is used for the preparation of tetrachlorvinphos : to a 50 g portion of 2,2,2′,4′,5′-pentachloro acetophenone, 25.5 g trimethyl phosphite is added within a period of 30 minutes, while the temperature is kept at 30—50 °C. The mixture thus obtained is heated to 110 °C for 30 minutes, whereupon it is cooled and mixed ether in order to start the separation of the precipitate. Tetrachlorvinphos was obtained with a yield of 79 %; the melting point of the product was 97—98 °C.

The most difficult step of the procedure according to the patent is the distillation of pentachloro acetophenone at a pressure of 0.05 Torr. Accordingly, the necessity of the distillation of pentachloro acetophenone was checked and it was found that the purity of the product depends, first of all, on the circumstances of the hydrolysis of the aluminium chloride complex. Conditions could be determined under which it is not necessary to distil the product, but it can directly be applied for the preparation of tetrachlorvinphos. The essence of the above-mentioned procedure is that the maximum temperature of hydrolysis, when making the complex to be decomposed, should be around 40 °C. A procedure for drying the water-containing raw pentachloro-acetophenone by azeotropic distillation was developed; the operation was carried out in a petrol solution and the remaining petrol solution can directly be used for the preparation of the active ingredient. From the solution remaining after condensation with trimethyl phosphite, the active ingredient is directly separated by cooling; its quality is not inferior to that of the product obtained from distilled pentachloro acetophenone.

In addition to determining the optimum parameters, corrosion tests were also carried out and the structural materials suitable for the individual technological processes were determined. Accordingly, the reactors, their fittings and accessories (condenser, and product recipient) should be of enamelled finish, whereas the pipelines, their fittings and the intermediate storage vessels are best made of stainless steel type KO-35.

The production process that was developed will be described in detail in the following. A reactor of 30 ℓ capacity, provided with an enamelled finish, was equipped with a stirrer of the speed of 100 r.p.m., a glass condenser and feeding funnel. 80 moles (9.86 ℓ) of technical-grade trichlorobenzene and 88 moles (11.76 kg) of technical grade aluminium chloride were weighed in and a slurry was produced therefrom by stirring the mixture for 5 minutes. Hereupon 80 moles (7.60 ℓ) of dichloro acetyl chloride were added within a period of 15—20 minutes. The reactor was carefully heated to 90 °C. The evolution of hydrochloric acid gas became intensive above 40 °C. The temperature was kept at 87—93 °C for 4 hours and thereupon the complex was discharged and slowly brought into an autoclave of 250 ℓ capacity, containing 120 ℓ water that had been cooled to 1 °C. The highest temperature observed in the course of the hydrolysis was 45 °C. After additional stirring for half an hour, the product was allowed to separate for 2 hours. Hereupon the oily liquid forming the lower layer was separated. The supernatant aqueous solution was discarded. The product was washed with 40 ℓ water of 45 °C temperature. After separation (the weight of the raw, water-containing product was 26.3 kg) the substance was returned to the reactor, mixed with 40 ℓ of a petrol fraction of an initial boiling point of 90 °C, and freed of water by azeotropic distillation. In this manner, 4.7 ℓ of water was removed by distillation and 21.6 kg of petrol solution was obtained. From the latter, 1.37 kg solid product was separated upon standing. This was separated by filtration and its pentachloro acetophenone content, or more exactly, the amount of trimethyl phosphite necessary for the condensation was determined by the thermoindication technique.

The above-mentioned techniques developed in this Institute, is based on the fact that the reactions in which technical pentachloro acetophenone is used up are highly exothermic. Consequently, when carrying out a titration under isothermal conditions using trimethyl phosphite as titrating reagent, the end-point can be indicated by cessation of the change in temperature. Thus to 10 litres of the petrol solution (according to our analysis, the petrol solution contained 62 % pentachloro acetophenone) a further portion of 5 ℓ petrol was added, and with cooling applied, so as to prevent the temperature rising above 50 °C, 20 moles (2.5 ℓ) of trimethyl phosphite were added with continuous stirring, within a period of about 50 minutes. Having finished the addition, the solution was heated to 110 °C in 25 minutes and kept at that temperature for 1 hour. The solution was, with continuous stirring, cooled to 15-20° in about 2 hours, and the separated product was removed by filtration. The filtrate was twice washed on the filter with 3 litre portions of petrol and dried at 70—80 °C. 5.4 kg of product was obtained, its melting point being 92°C, and its purity 98.1 % (by gas chromatography); accordingly, the yield was 72 %, as calculated on trimethyl phosphite.

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РЕЗЮМЕ

Действующим началом инсектицида марки "Гардона" является тетрахлор-винфос, получение которой было авторами изучено в прошлых годах в лабораторном, затем и опытно-заводском масштабе. Отечественное производство данного средства обосновывалось литературными данными по преимущественному спектру его действия и весьма низкой ядовитости для теплокровных, а также и по простому его получению.

При исследованиях были авторами установлены оптимальные условия реакции Фридл-Крафца для 1,2,4-трихлор-бензола и дихлор-ацетил-хлорида. Полученный при этом пентахлор-ацетофенон был высушен азеотропной дистилляцией, а конденсация с триметил-фосфитом была выполнена в легком бензине. Из бензинового раствора при охлаждении выделялось сырое техническое действующее начало, которое после промывки и высушивания можно формировать.

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ERRORS IN THE MEASUREMENT OF HEAT QUANTITY TRANSMITTED BY STREAMING LIQUIDS

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During studies concerning measuring instruments that are qualified for the determination of the quantity of heat transmitted in a given system by a streaming liquid, it was shown - in addition to a description of the errors of the usual measuring instruments - that the latter are burdened by a systematic error originating from their operating principles. After a detailed examination of the "delay time", the cause of systematic error, and the principal layout of the QM-221 type digital heat quantity measuring instrument are presented. The instrument developed at the NEVIKI - is free of the error mentioned.

In addition to the temperature, pressure, flowing quantity and other physical and chemical parameters, an important characteristic in chemical, pharmaceutical and energy industries - as well as in other industries, producing or consuming thermal energy - is the quantity of heat transmitted.

The present paper deals with the errors of heat quantity measurements and the methods aimed at decreasing these errors in the case of instruments capable of measuring the quantity of heat introduced into or removed from a system. The principle of the measurement is illustrated in Figure 1. The NEVIKI QM-121 type digital heat quantity measuring instrument also operates along this principle.

This instrument measures the $O_{in}(t)$ input temperature, the $O_{out}(t)$ output temperature and the $V(t)$ volumetric flow rate of the flowing medium. The heat quantity absorbed or released by the system can be determined on the basis of the following Equation:

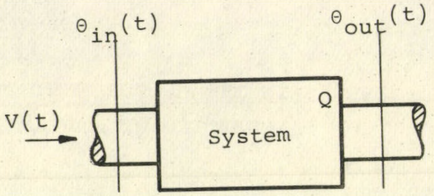

Fig.1. Principle of the measurement of the heat quantity transferred or taken up by the liquid flowing through the system

$$\frac{dQ}{dt} = 3600.V(t).\gamma .c.\Delta\theta(t) \quad [kcal/h] \qquad (1)$$

whereas the heat quantity absorbed or released by the system during a time t_1 is determined by Equation:

$$Q = c.\gamma.\int_0^{t_1} V(t).\Delta\theta(t)dt \quad [kcal] \qquad (2)$$

The following conditions mus be fulfilled in the measurement of heat transfer:

1. No process involving the liberation of heat (e.g. change in state, and chemical reaction, etc.) may occur in the heat transfer medium.
2. The specific heat and the density of the heat transfer medium can be regarded as constant, or their temperature dependence can be ignored by considering a mean value. It is apparent from the functional equations that the E_Q error of the instruments is composed by two components:

   - the error of flow measurement (E_V)
   - the error of temperature measurement (E_θ)

in the following manner:

In practice, this value usually varies in the 1 to 5 % range. Generally, the error E_V of the flow measurement cannot be influenced; it is a value characteristic of the flow meter, as specified by the manufacturer, generally 0.5 %. The error of the temperature difference measurement can be influenced by linearization of the characteristic curve of the heat sensing element (e.g. platinum).Considering the aforesaid, an accuracy of 0.5 % could be attained by this method; however, it is self-evident that the method can be applied only in a stationary state and when also taking the time dependence of the $\Theta_{in}(t)$ input temperature into consideration it becomes apparent that in a transient state the method is burdened with a systematic error, if the value of Θ is calculated as the difference of Θ_{in} and Θ_{out} values measured at the same time. Naturally, the systematic error disappears or is limited to a known error value if Θ_{in} is constant or can be regarded as constant within a given margin of error. Similarly, the heat quantity calculated from simultaneously determined Θ_{in} and Θ_{out} values is lower than a known limiting error value, if the measuring interval is a large multiple of the delay (transport) time, i.e. of the time needed for a volume element of the liquid to pass the system. The error is no larger than the error made at the intervals corresponding to the first and the last delay time.

The systematic error is eliminated if the temperature of the same volume element of the liquid will be measured both at the input and the output, and the difference in these temperatures will be applied for the calculation of the heat quantity. However, the solution of this task is not simple, especially because the delay (transport) time is a function of the $V(t)$ volumetric flow rate. The problems connected with and the solution of the general case is presented in Figure 2.

The Figure shows the input and output temperature of the flowing medium of the heat transfer system, plotted against time. The delay (transport) time was chosen as the time unit. Curve Θ_{in} shows variations in the input, and curve Θ_{out} those in the output temperature, both in accordance with time scale ①. Curve Θ'_{in} is shifted compared to curve Θ_{in} by the transport time T (time scale ② . The temperature differences free of systematic error are obtained as the differences of the Θ'_{in} and the Θ_{out}

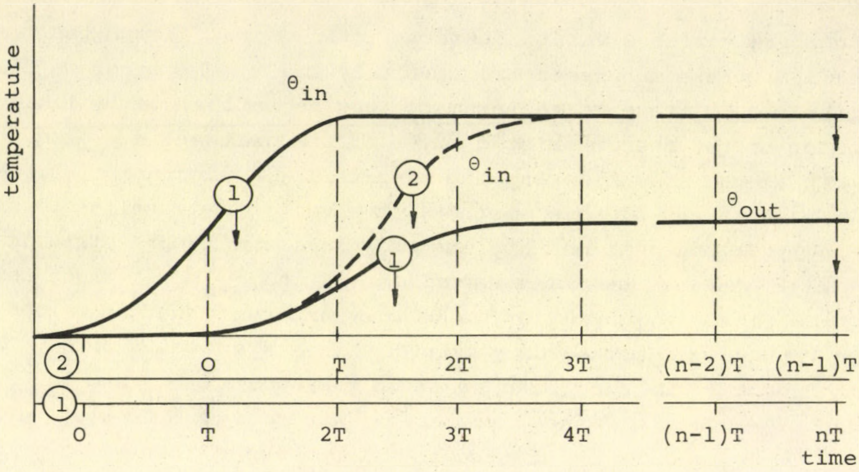

Fig.2. Time dependence of temperatures θ_{in} and θ_{out}, measured at the input and output points, respectively, of the system. θ_{in} and θ_{in} corrected with the delay time (T).

values pertaining to the same abscisse value.

The mathematical model corresponding to the considerations described in the foregoing can be constructed on the basis of Figure 3.

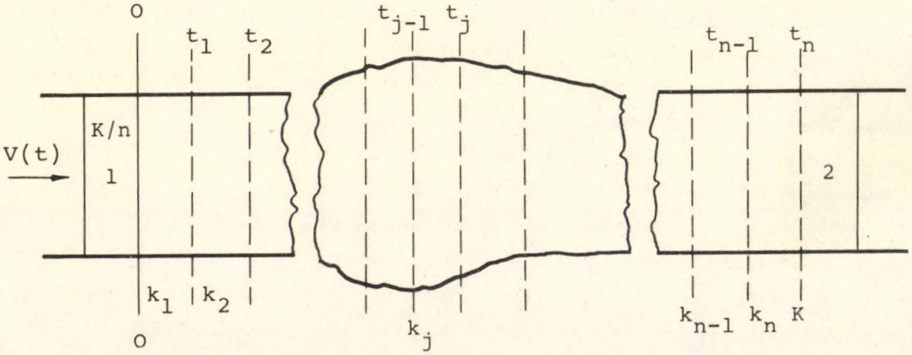

Fig.3. Elimination of the systematic error brought about the delay time.

The system according to Figure 3 is a tube section not necessarily but without any branching off. There are two temperature sensors at cross sections"O" and "K", where:

K	is the volume of the system between O and K
K_j	is one volume element of the system
V t	is the volumetric flow rate of the liquid flowing through the system

and it is assumed that the liquid is incompressible, i.e. its volumetric flow rate "V (t)" is identical at any cross section of the system, moreover the mixing and heat transfer in the direction of flow are neglected. The volume elements are chosen so as to have:

$$k_1 = k_2 = \ldots k_n = \frac{K}{n} = k \tag{4}$$

in which case we can write:

$$K = \sum_{j=1}^{n} k_j = n \cdot k \tag{5}$$

The volume element designated by "1" in the Figure 3. of the volume K/n is transferred to the volume element designated by k_1 if the following Equation is true:

$$k_1 = \frac{K}{n} = \int_{o}^{t_1} V(t)\, dt \tag{6}$$

and, in general, from the "j"-th volume element to the "j+1"-th one, if Equation:

$$k_j = \frac{K}{n} \int_{t_{j-1}}^{t_j} V\,(t)\, dt \tag{7}$$

holds.

The liquid is presumed to be incompressible and consequently Equations(6)and(7)also mean that a liquid of unit volume enters at point "O" and is descharged at point "K" at the same time.

If the "$V(t)$" volumetric flow rate of the flowing liquid is sensed at an optional point of the tube section and the signal furnished by the sensor is used to produce the "k_j" values on the liquid in position "1" to be transferred into position "2" can be expressed; this happens, when a volume

$$\sum_{j=1}^{n+1} k_j = (n+1)\,k = K + \frac{k}{n} \qquad (8)$$

of the liquid has passed through the system, or, of the frequency of the passing of unit volumes is counted, after the "n+1"-th step.

Accordingly, if the measuring system operates in such a manner that the enthalpies of the unit volumes passing through the input are determined and the values thus obtained are stored in their sequence, and the enthalpies of the unit volumes at the output are also determined and each value of the latter set is compared to that of the former set preceding it by "n+1" steps, the algorithm described as the aim in the introduction has been realized.

If the liquid volume elements passing the output of the system are counted with index "i", the following Equation may be written for the value of the sum:

$$\Delta Q_i = c \cdot \gamma \frac{K}{n} \left\{ \Theta_{in\,[i-(n+1)]} - \Theta_{out\,(i)} \right\} \ [\mathrm{kcal}] \qquad (9)$$

and for the instantaneous values:

$$\frac{\Delta Q_i}{\Delta t} = \Delta Q_i \, \frac{3600}{t_i - t_{(i-1)}} \ [\mathrm{kcal/h}] \qquad (10)$$

However, since:

$$t_1 - t_{(i-1)} = \frac{k_i}{V_i} = \frac{k}{V_i} = \frac{K}{nV_i} \qquad (11)$$

Equation (10) can be brought to the following form:

$$\frac{\Delta Q_i}{\Delta t} = 3600.c.\ \gamma.V_i \left\{ \Theta_{in\,[i-(n+1)]} - \Theta_{out\,(i)} \right\} [\mathrm{kcal/h}] \qquad (12)$$

Equations (7), (9), (11) and (12) represent the functional Equations of the heat quantity measuring device operating on the basis of a delay algorithm. From among these, it is Equation (7) that the functioning of the flow meter and of the integrator coupled to it in the general case. The output signal of this unit gives the frequency of the passage of the liquid elements of unit volume. In practice, this is most preferably realized by a turbine-type flow-meter with a counter connected to it.

The above model eliminates the systematic error brought about by simultaneously measured input and output temperatures; however, it unvariably is burdened by random errors and, furthermore, by the error of the measurement of the new parameter appearing in the new model, the volume of the system (K) as well as by errors originating from neglections taken in establishing the model (assuming incompressibility, neglecting the possibility of air pockets; mixing and heat transfer in the direction of propagation).

This error analysis presents the possibilities of application and limitations of heat quantity measuring devices that today can be called classical; at the same time, it defines those measuring assignments where it is preferable to apply the new heat quantity meter capable of eliminating the systematic error brought about by the delay time. It has so far not been discussed, but nevertheless it is self-evident that - for all tasks, where the parameter to be measured is $\frac{\Delta Q}{\Delta t}$ the heat quantity transferred during unit time, it is the new technique that supplies a more adequate information.

The development of the QM-221 type digital heat quantity meter at the Department of Air Pollution Control and Control Engineering of the NEVIKI Institute is almost concluded. The instrument is capable of eliminating the transport error and at the same time, it solves the linearization of the response of the platinum resistance thermometer. A detailed description of the instrument is not presented here, it is sufficient to remark that it is of micro-programmed design and also contains a channel-controller unit which enables it to be connected to a computer.

Symbols used

Q	heat quantity, [kcal]
t	time [s]
v	volumetric flow rate of flowing liquid $[m^3\ s^{-1}]$
$V(t)$	volumetric flow rate as a function of time t $[m^3\ s^{-1}]$
Θ	temperature $[^{o}C]$
$\Delta\Theta(t)$	temperature difference as a function of time t $[^{o}C]$
γ	density of flowing liquid $[kg/m^3]$
c	specific heat of flowing liquid $[kcal/kg\ ^{o}C]$
E_Q	error of the instrument
E_V	error of flow measurement
E_o	error of temperature measurement
K	volume of the system between O and K $[m^3]$
k_j	one volume element of the system $[m^3]$
k_i	one volume element of the flowing liquid $[m^3]$
$\Theta_{out(i)}$	output temperature of i-th liquid volume element $[^{o}C]$
$\Theta_{in[i-(n+1)]}$	input temperature of same liquid volume element $[^{o}C]$
Q_i	heat quantity transferred to (taken up from) the system [kcal]
t_i-t_{i-1}	time of passage of i-th volume element from volume element "n" to volume element "n+1+ [s]
n	number of elementary volume elements of the system
V_i	volumetric flow rate during passage of the i-th element $[m^3.s^{-1}]$

РЕЗЮМЕ

Предметом сообщения является исследование ошибок измерительных установок пригодных к определению количества теплоты, передаваемой текущей жидкостью в определенной системе. После ознакомления читателей ошибками традиционных измерительных установок показывается авторами, что последние погружены систематической ошибкой, происходящей из принципа их работ. После подробного изучения так называемого времени задержки, вызывающего систематическую ошибку, описано авторами принципиальное устройство измерительного прибора количества теплоты типа QM-221 , исключающего упомянутую выше ошибку измерения и находящегося ныне в стадии разработки в Исследовательском Институте Основной Химической Промышленности.

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HIGH ACCURACY DIGITAL/ANALOGUE CONVERSION

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The most important applications of digital/analogue conversion in chemical engineering are briefly summarized.

After this summary, the mathematical model of the D/A converter developed at NEVIKI LIFO is described; the factors influencing the accuracy of the D/A converter are discussed on the basis of the model.

The field of application of D/A conversion mentioned in the title as well as that of D/A converters is rapidly expanding. Instead of presenting an enumeration of all the possible applications, an example taken from the narrower field of operation of this Institute will be applied for the verification of the above statements and for summing up the present situation.

The example comprises on-line computer control of a continuous chemical industrial technology; the latter can be characterized by the general flow diagram presented in Figure 1. There is a part of continuous operation in time, comprising the process proper and the part of the control device operating in an analogue manner, and there is an other part of discrete operation, comprising the computer and the auxiliary units necessary for its operation.

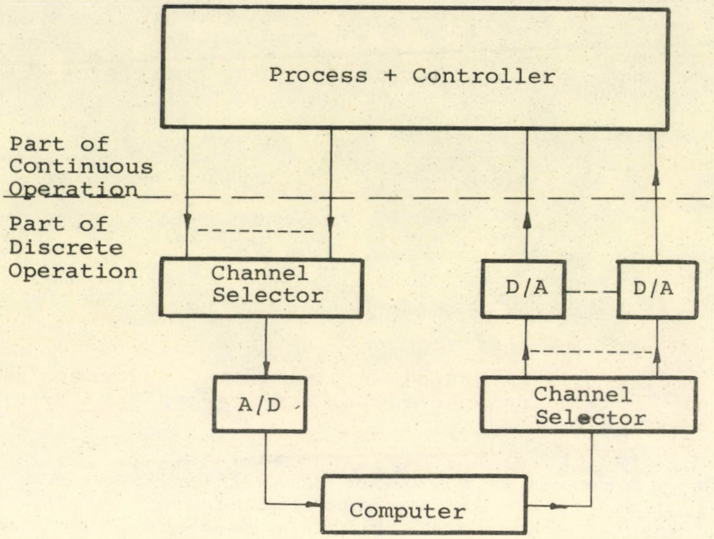

Figure 1. General flow diagram of the computer controlling of a chemical engineering process

The computer obtains information on the continuous-operation part of the system at discrete time instants and it sends information, similarly at discrete time instants, towards the controller governing the process. In addition to the selection of the adequate channel, two signal transformations are necessary for this exchange of information. First the analogue signals of the sensors have to be transformed into digital signals, understood by the computer, this process being termed analogue/digital conversion. Secondly, the digital information supplied by the computer has to be reconverted for the controller, this being digital/analogue conversion. Accordingly, a D/A converter transforms a digital signal into an analogue one. The digital signal is in the present case a binary or binary coded numeral, whereas the analogue signal is a voltage or a direct current.

As it is apparent from the above example, in addition to their other fields of application, D/A converters are also important elements of on-line control systems; in fact, even a medium-size on-line control system needs a fair quantity of them (generally as many as 10—20). It is characteristic of the D/A converters available at present that their design is complicated, they are constructed of special or carefully selected components and consequently their production and calibration is time consuming and cumbersome.

In the following, a description of the D/A converter designed at NEVIKI is presented. This converter overcomes the drawbacks described in the foregoing. The design of this D/A converter, from the point of view of systems engineering, is shown in Figure 2. The digital information to be converted - designated by N in the Figure - is conducted to one input of a digital comparator, whereas the other input of the latter is connected to a counter which continuously counts the pulses of a free running oscillator.

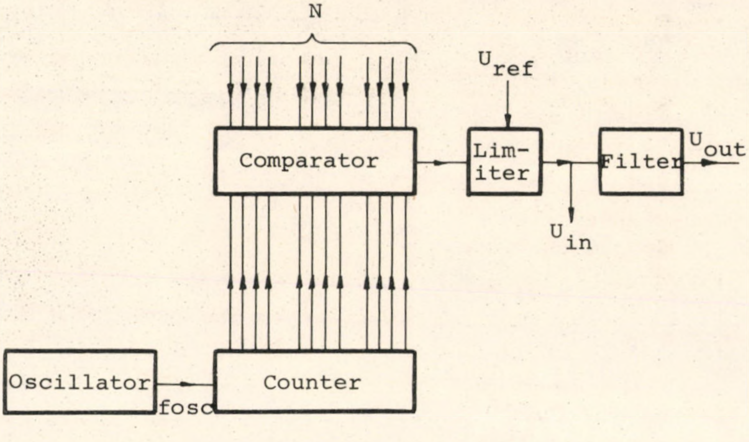

Figure 2. Design of the D/A converter from the point of view of systems engineering

The comparator compares these two signals and at its output there is a logical level of 1 as long as the content of the counter is lower than or equal to N and there is a logical level of 0 if the content of the counter is higher than N. Accordingly, the content of the counter periodically increases from zero to a maximum value determined by the capacity of the counter and it reaches and surpasses the value of N in every cycle. Consequently, a periodic square wave signal is produced at the output of the counter. This square wave signal is brought to a uniform shape by a limiter stage in such a manner that its amplitude is either U_{ref} or zero. The shaped signal is hereafter brought to a low pass filter at the output of which a DC voltage proportional to N appears.

In order to construct the mathematical formulae describing the operation of the converter let us start from the periodic square wave signal designated by U_{be}, applied to the input of the filter. It is easy to draw this square wave signal on the basis of the aforesaid (Figure 3). The figure shows the time function of the square wave signal applied to the input of the filter. The cycle of this signal is designated by T. If the capacity of the counter is designated by C, and the time of one cycle of the oscillator signal by τ, we can write $T = C\ \tau$. U_{ref} designates the accurate reference voltage and N the number to be converted. The Equations characteristic of the operation of the converter can be obtained from the Fourier-series of this signal.

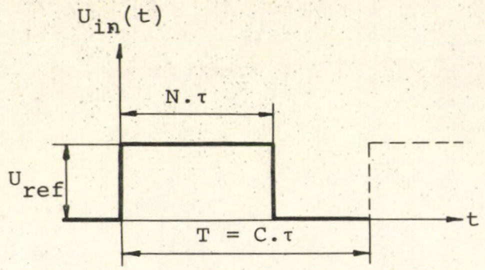

Figure 3. Time function of the input signal of the filter

$$U_{in(t)} = \frac{U_{ref}}{C} N + \sum_{k=1}^{\infty} A_k \cdot \sin(k\omega t + \varphi_k) \qquad (1)$$

where

$$A_k = \frac{U_{ref}}{k\pi} \sqrt{1 - \frac{C\ \tau}{k\ \pi} \cos\left(\frac{2\pi \cdot k \cdot N}{C}\right) + \left(\frac{C\ \pi}{k \cdot 2\pi}\right)^2} \qquad (2)$$

$$A_{k\ max} \approx \frac{U_{ref}}{k \cdot \pi} \qquad (3)$$

$$\varphi_k = \text{arc tg} - \frac{\sin\left(\frac{k \cdot 2\pi \cdot N}{C}\right)}{\cos\left(\frac{k \cdot 2\pi \cdot N}{C} - \frac{C\pi}{k \cdot 2\pi}\right)} \qquad (4)$$

$$\omega = \frac{2\ \pi}{T} = \frac{2\ \pi}{C \cdot \tau} \longrightarrow f_1 = \frac{f_{osc}}{C} \qquad (5)$$

The Fourier series is shown in the upper line, whereas the coefficients A_k and φ_k are shown below. It can be concluded on the basis of the series that the component of zero frequency (f_o, the first term in the series) is proportional to N, i.e. if the filter cuts off all the upper harmonics - which are given by the expression after the summation sign - the network structure described above is able to perform D/A conversion. The further Equations are necessary for dimensioning the filter; these will not be described in detail here. Instead, the frequency spectrum - or, more exactly, the location and maximum amplitude of the harmonics - as determined from the Fourier series, are presented in a Figure (Figure 4). Accordingly, the task of the filter is to transmit the component of 0 frequency and to cut off all

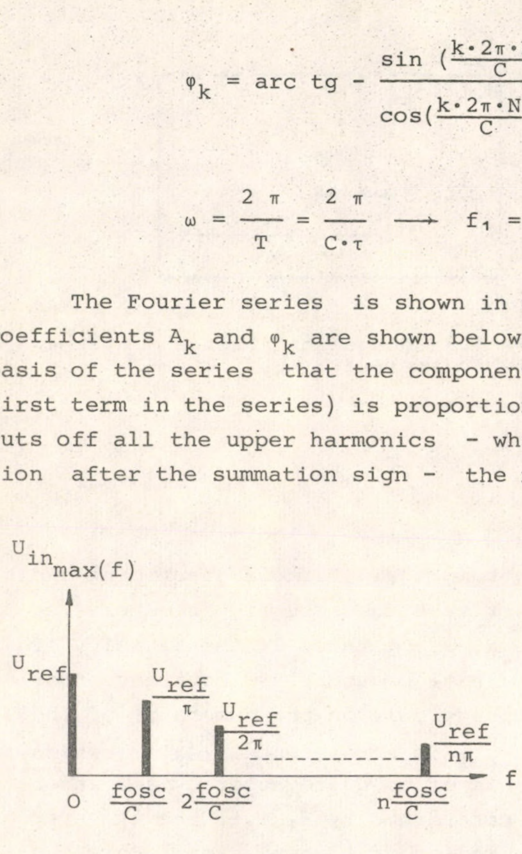

Figure 4. Frequency spectrum of the input signal of the filter

other frequencies. It is apparent from the Figure that the amplitude of the upper harmonics decreases as a monotonic function and consequently it is sufficient to design the filter for the second harmonic and prescribe its damping for this one, i.e. the f_f break point frequency of the filter has to be selected adequately lower than the frequency - f_1 - ot the second harmonic.

The final result is presented in Figure 5 which shows the connection between the input and output signal of the filter. The Bode diagram of the filter characteristics, determined according to the aforesaid, is drawn into the Figure. On the basis of this diagram, the final form of the output voltage of the filter can be written; this is, at the same time, the output voltage of the D/A converter.

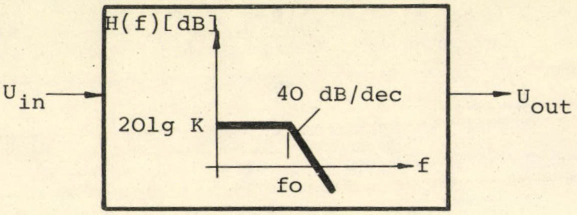

Figure 5. Connection between input and output signal of the filter

$$U_{ki} = \frac{U_{ref} \cdot K}{C} N; \qquad f_f \ll f_1 \qquad (6)$$

It can be concluded from the mathematical formula describing the output signal of the D/A converter that the accuracy is determined by the fraction standing before N. From this, C, the capacity of the counter is an absolutely definite constant without any error and accordingly the error depends only on the numerator of the expression. From the numerator, U_{ref} is a reference voltage which - when appropriately designed - is of adequate accuracy and accordingly the error is principally determined by K, i.e. the transfer coefficient of the filter in the region of transmission. This can also be brought to an adequate accuracy.

Finally it can be concluded that the output signal of the D/A converter is influenced by only a few parameters, moreover, all of these can be selected appropriately and consequently an accuracy of 0.1 %, or even 0.01 % can be reached, as was originally aimed at.

РЕЗЮМЕ

В работе дан краткий обзор важнейших применений в химической промышленности конверсии цифровых величин на аналоговые. Далее автором описана математическая модель цифрового-аналогового конвертера, разработанного в Исследовательском Институте Основной Химической Промышленности, и на основе модели изложены факторы, оказывающие влияние на точность цифрового-аналогового конвертера.

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FIVE-PARAMETER MICRO-CLIMATIC MEASURING STATION

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The micro-climatic measuring station is capable of performing, simultaneously with the determination of harmful air polluting components, the measuring and recording of five meterological parameters (atmospheric temperature, humidity, absolute barometric pressure, wind velocity and direction). The apparatus can be regarded as a hybrid single-purpose computer, because it optimally combines a high-precision analogue measuring technique with the considerable resolving power of digital technique.

One of the basic and vitally important elements of human environment is air. The earth is surrounded by $6x10^{15}$ tons of air and the filling of this vast amount with pollutants is, according to various opinions, impossible. However, the pollutants are not distributed evenly in the atmosphere. The presence of air pollutants at the one-millionth level may be very harmful to the organism. Consequently, the determination of the distribution of air pollutants in space and in time is of major importance. In addition to the concentration of air pollutants, determination of their propagation also represents very important information.

The Department for Air Pollution Control and Control Engineering of the Research Institute for Heavy Chemical Industries (NEVIKI LIFO) developed the DAPOMAC NORX 211 data collection equipment for the purpose of air purity control. The equipment enables complex measuring tasks to be solved. Simultaneously with the measurement of air polluting components, the meteorological characteristics of the environment (micro-climate) of the measuring station also can be determined. The micro-climate parameters present information on the propagation of the air pollutants; furthermore, they are of importance in connection with the repeated determination of the data.

Electronic circuits coupled as accessories to the data collection equipment enable the determination of the following meteorological parameters: air temperature, humidity, absolute barometric pressure, wind velocity and direction.

Technical Probleme of the Measurements

The meteorological parameters were determined simultaneously with the measurement of the polluting components, with the application of measuring techniques that are usual in meteorology. The measurement of the atmospheric parameters was not aimed at determining the micro-climate in the meteorological sense. The data obtained are of importance from the viewpoint of the pollution control. In the case of repeated measurements, micro-climatic changes in the given environment and their effect upon the distribution of the pollutants present in the atmosphere can be taken into consideration.

The measuring range and accuracy of the instruments enabling the measurement of meteorological parameters are fixed by international regulations and recommendations. The measuring range and the accuracy are determined by the transducers (transmitters). The transducers used in the present work transfer non-electrical quantities (e.g. wind velocity) into electrical signals with the prescribed degree of accuracy.

The information content of the measured values is also of importance. Accordingly, the measuring equipment is capable of presenting the instantaneous, mean and integrated value of the information obtained from the source of information. The user can decide which value to use in his calculations.

In a complex measurement carried out in a given environment, the amount of the measured data is very large. The manual processing of a large amount of data is time-consuming and consequently computer processing of the data has to be provided for. However, it is often necessary to draw certain conclusions while the measurements are in progress and partial results - integrated or mean results pertaining to a certain time - are necessary for this purpose. In on-line computer processing of such data is no problem; however, a computer is not always available or not at the given instant, and consequently in the case of automatic data recording it is preferable to equip the measuring station with an arithmetic unit and a adequate capacity memory. In this way, it is possible to acquire partial results even while the collection of the data is in progress.

The recording of the data supplied by the measuring system is carried out by a tape puncher combined with an electric typewriter. This enables the checking of the measured results, while the data are being collected. The figures recorded on the punched tape can be processed by a computer, by means of an appropriate mathematical programme.

Measuring Methods and Transducers

The non-electrical quantities to be measured are transformed by transducers (transmitters) to an electrical quantity for the electronic unit. This transformation may be analogue or digital.

In analogue transformation, a current proportional to the quantity to be measured and changing in the range 0 ... 20 mA is obtained.

In digital transformation, a series of discrete pulses or a position-code is obtained.

Temperature measurement. The measurement of atmospheric temperature is carried out in an analogue manner, by the application of a Pt 100 DIN type resistance thermometer. The main characteristics of the platinum resistance thermometer are the following: relatively high temperature coefficient, a resistance value constant in time and well reproducible in production. In the transmitter developed in this work, a double-thermometer system was applied. The advantage of this system is that transformation is linear in the -30 to +50 °C temperature range. It can be verified both by calculation and measurement that the error induced by the thermal radiation of the environment of the sensor is a multiple of those originating from causes of electrical origin. Consequently the resistance thermometer was surrounded by a protective screen.

Measurement of air humidity. The humidity content of the air is determined on the basis of the psychrometric difference. The transformation is of an analogue nature. The psychrometric measuring technique is based on the high heat of the evaporation of water. The air sample to be examined is made to pass a resistance thermometer surrounded by moist material and two other ones surrounded by dry material. The resistance of the moist thermometer is decreased on account of heat loss. The absolute or relative humidity content of the air can be calculated from the psychrometric difference of the moist and dry thermometers.

Barometric Pressure Measurement. The pressure measurement is based on an analogue transformation.Changes in barometric pressure bring about minute movements of a membrane chamber. A ferrite core, secured to the membrane chamber, moves in a coil excited with an AC current. At the movement of the core, the mutual induction coefficient of the coil system changes. After rectification, an output current proportional to the pressure is obtained.

Part of the analogue transducers described in the foregoing is a commercial construction. A measuring head for the measurement of wind parameters that can be coupled to the data processor was developed in the Institute. Commercial measuring heads could not have been used without considerable modification.

Measurement of Wind Parameters. The wind velocity and wind direction transmitters are of identical mechanical design. Transformation is digital. The wind velocity transmitter is essentially a turbo-type anemometer. In the wind direction transmitter, the sensing of the direction with reference to the points of the compass is carried out by a wedgeshaped wind flag. The rotation of the wind velocity meter and the instantaneous wind direction are forwarded to a code disc by a magnetic clutch. The marks, brought upon the code disc in 4-bit Grey code, are transilluminated by photoemitting diodes. In the wind velocity measurement the pulse number per unit time is obtained, whereas in direction measurement the angular rotation, with an accuracy of 1/16 of the points of the compass.

Description of the Complex Measuring Station

A data collection and recording apparatus, also suitable for the purposes of air pollution control - DAPOMAC NORX 211 (DIGITAL AIR POLLUTION MEASUREMENT AND CONTROL) was completed in this Institute in 1973. The equipment is capable of performing the following assignments:

- it is compatible with the instruments used in air pollution control and in addition to industrial selfcontrol it enables the automation of the measurements carried out in any field and the recording of the data thus obtained;
- it transforms analogue electric signals, with the application of an input driver, into impulses corresponding to the 0--1000 mV range, and thereupon, by means of a high-precision analogue--digital converter (digital voltmeter) it displays them in digital form;
- the digital signals are, with application of a Signal shaper, stored in a number chain of the capacity 10^5 during the selected period of measurement;

- in predetermined time instants, the time of the measurement, the denomination of the measuring places and the results of the measurements are printed (or punched on a tape);
- the operators carrying out the series of measurements are continuously kept informed of the measurement process by a special "dialled result display" operation mode;
- by merit of the built-in arithmetic unit, it is capable of producing mean values or extreme values;
- the basic unit enables the measurement and recording of signals arriving through 32 analogue or digital channels;
- data recording on tape puncher, electric typewriter, telex, or teletype;
- in order to perform different measurement tasks, additional measuring circuits can be connected to the measuring equipment.

Setup of the Micro-Climate Measuring Station

The block diagram of the micro-climate measuring station is represented in Figure 1. The sensors are, in the case of analogue

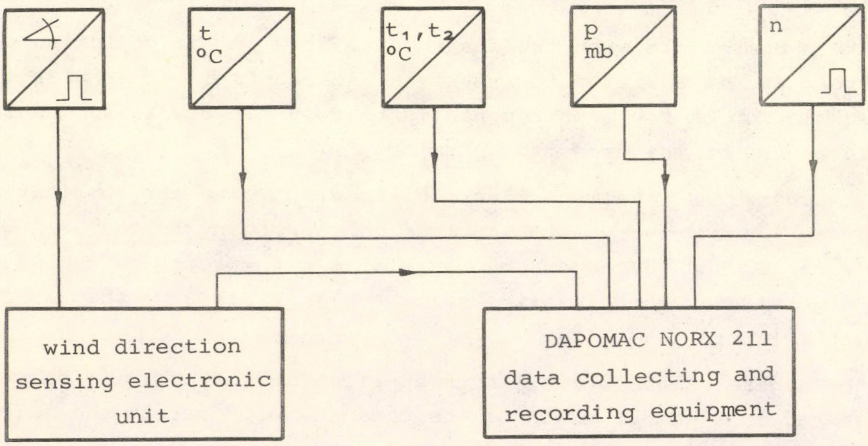

Figure 1. Micro-climatic measuring station equipped with a DAPOMAC NORX 211 type data collector. 1 - wind direction sensing electronic unit; 2 - DAPOMAC NORX 211 type data recording equipment and collecting equipment.

signals, connected galvanically, in the case of pulse transmitters by photo-electric coupling to the data processing equipment. The values measured during the sampling periods selected by the operators are integrated by the data collecting and recording equipment.

Electronic Unit Processing Wind Direction Data. The electronic unit carrying out the processing of wind direction data is an accessory of the DAPOMAC NORX 211 apparatus. Its main functions are the following: determination of the wind direction most frequently occurring during the sampling period and the determination of the instantaneous values of a given direction in degrees. The resolving power of the wind direction transmitter is 22.5°, which corresponds to 1/16 of the points of the compass. The following angular positions were assigned to the main direction of the compass: North = 360°; East = 90°; South = 180°; West = 270°. The display of the 16 directions obtained by the 22.5° resolution is carried out by a 4-bit Gray code disc. By transformation of the 4-bit Gray code into a binary number, a binary address can be assigned to every 1/16 direction. The position of the angle transmitter is checked every 15 seconds. In a sampling time of 30 minutes, this means 240 samples. The number of occurrences of the measured directions is stored in a memory bank. After the sampling period, the electronic unit, in its extreme value seeking phase, examines the contents of each memory section and notes the sum of the maximum contents. The multiplication corresponding to the noted sum is carried out by the arithmetic unit. The result of the multiplication is a binary number, which is made suited for display and recording by the binary-decimal converter. After the printout phase the content of the memory is zeroed.

The measuring station described in the foregoing was primarily designed for the purpose of air pollution control; however, it solves measurement and evaluation problems occurring not only in air pollution control. Its design enables any high-frequency industrial or laboratory measurement to be carried out with the equipment.

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РЕЗЮМЕ

Микроклиматической измерительной станцией выполняется одновременно с определением вредных компонент, загрязняющих воздух, измерение и регистрация пяти метеорологических параметров (температура воздуха, влажность и абсолютное давление воздуха, скорость и направление ветра). Данную установку можно считать целевой ЭВМ, так как она оптимально соединяет в себя аналоговую измерительную технику высокой точности с высокой разлагающей способностью цифрового измерения.

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RELATIONS ENTRE LES CARACTERISTIQUES ELECTROCHIMIQUES DES ALLIAGES ET LA TENDANCE A LA CORROSION PAR PIQURES

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On a examiné par voie potentiostatique et chronopotentiostatique la tendance à la corrosion par piqûres de divers aciers austénitiques,dans des solutions aqueuses, contenant des chlorures et des acides organiques communiquant a l'air. On a étudié les valeurs de certains paramètres éléctrochimiques des alliages susceptibles à la corrosion par piqûres et celles des alliages qui sont exempts de cette tendance. On a observé des relations qualitatives et générales entre les propriétés et les paramètres électrochimiques des alliages. En partant de ces bases on peut comparer la tendance relative à la corrosion par piqûres, dans tous les cas. Pour qualifier toutefois certains alliages on doit avoir plusieurs paramètres précisément définis. Après avoir défini le potentiel de rupture, on peut bien profiter l'essai chronopotentiostatique fait au potential convenablement choisi.

INTRODUCTION

Ceux, qui ont étudié le processus de la corrosion par piqûres, sont nombreux, d'une part à cause de l'importance pratique, d'autre part de son interêt théorique. Le problème principal provient de ce que des endroits se corrodants très vite et des endroits exempts de la corrosion existent simultanément a la surface du métal.

Un partie des études traite le mécanisme du processus et les facteurs, qui influencent le processus (1-8), l'autre partie de celles traite l'influence des composants d'alliages et de solution (9-19).

La différence des propriétés de celles de la corrosion uniforme nécessite l'analyse complémentaire des méthodes expérimentales à appliquer. Les méthodes d'immersion antérieurement appliquées avaient des inconvénients, et exigaient du temps d'études bien long.Le point de départ des méthodes électrochimiques c'est l'observation de BRENNERT (20), qui a constaté le premier, qu' il est possible de déterminer la tendance à la corrosion par piqûres d'un acier allié dans un milieu de chlorure stagnant aux potentiels, où l'intensité du courant, avec la polarisation simultanément produite, montre une augmentation brûsque.*

Jusqu'au potentiel de rupture, E_R l'acier ne corrode pas, mais à un potentiel plus positif, dans une solution contenant de chlorure, elle subit une corrosion par piqûres. La résistance à la corrosion de l'acier dépend donc du potentiel stationnaire (E_C) qui peut atteindre la valeur du potentiel de rupture. La valeur possible du potentiel stationnaire est décisivement déterminée par le potentiel d'oxido-reduction de la solution parce qu'il y a une relation fondamental entre les deux valeurs:

$$E_C \leqslant E_{Redox}$$

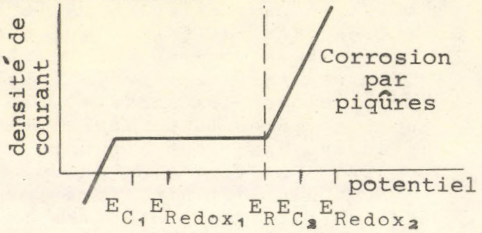

Fig.1. La relation parmi le potentiel de rupture, potentiel stationnaire, le potentiel oxydo-réduction.

Sur la figure 1. on représente la forme schématique des diagrammes de densité de courant - potentiel des aciers inoxidables, dans des solutions neutres ou faiblement acides. Il est évident, que

$$E_{Redox_1} < E_R, \text{ c'est à dire } E_{C_1} < E_R$$

Dans ce cas la corrosion par piqûres est exclue. Par contre en cas de

$$E_{Redox_2} > E_R$$

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*Selon certaines études (22) le potentiel de rupture n'est pas caracterisé par un potentiel bien précisé, mais par un intervalle étroit de potentiel,où l'adsorption des ions activants est bien forte.

E_{C_2} peut atteindre le domaine du potentiel de la corrosion par piqûres.

Pour déterminer la valeur du potentiel de rupture et des autres caractéristiques électrochimiques des alliages, les méthodes à appliquer sont les procédés galvanostatiques et le tracement des courbes de potentiel - temps (23). Les méthodes plus précises sont les mesures potentiostatiques et potentiocinétiques (24-28). Les méthodes appliquées sont très variables, parmi lesquelles surtout la vitesse du changement de potentiel influence considérablement les valeurs obtenues (29, 3o). Certains auteurs ont appliqué des examinations chronopotentiostatiques à un potentiel constant pour déterminer la tendance à la corrosion par piqûres et ils ont analysé la considération pratique des caractéristiques obtenues par les méthodes différentes (26, 31-33). Pourtant il semble, que l'analyse de la tendance à la corrosion par piqûres, le rôle des caractéristiques électrochimiques n'est pas determiné unanimement.

CONDITIONS EXPERIMENTALES

Pour déterminer les relations entre la caractéristiques et les propriétés corrosives nous avons fait de différents examens électrochimiques. D'abord nous avons tracé des courbes de polarisation potentiostatique par une vitesse de changement du potentiel relativement grande, 50 mV par 2 minutes. Nous avons dirigé le changement du potentiel toujours dans le sens positif. Avant le tracement des courbes les échantillons étaient activés au potentiel -600 mV (E.C.S.).

Plus tard, nous avons fait des examens chronopotentiostatiques au potentiel +100 mV (E.C.S.). On a fait un examen durant de 3o minutes en registrant simultanément les valeurs de la densité du courant.

Nous avons déterminé des potentiels stationnaires, des potentiels d'oxydo-réduction, et on a fait des observations visuelles.

Tableau 1

La composition chimique des alliages examinés

Le signe	Les éléments alliants, en pourcent										
de l'alliage	C	Cr	Ni	Mo	Ti	Nb	Mn	N	Si	S	P
A	0,05	17,30	12,90	2,40	-	-	1,25	-	0,48	0,020	0,028
B	0,06	17,46	14,50	4,55	-	-	1,28	-	0,59	0,021	0,027
C	0,07	17,81	16,50	-	0,35	-	1,60	-	0,63	0,014	0,023
D	0,05	17,64	11,98	-	-	-	1,51	-	0,53	0,015	0,027
E	0,06	18,19	16,89	-	-	-	1,31	-	0,52	0,016	0,025
F	0,07	17,30	6,35	-	-	-	6,88	0,19	0,47	0,022	0,026
G	0,06	18,16	5,92	-	-	-	9,67	0,15	0,39	0,023	0,029
H	0,06	17,83	8,75	-	0,41	-	1,40	-	0,44	0,024	0,014
K	0,04	17,50	13,10	2,49	-	1,03	1,14	-	0,52	0,028	0,015

On a pratiqué ces déterminations sur des alliages d'aciers austénitiques variés. Nous avons précisé la composition chimique des aciers par le tableau 1. Il y a 3 alliages contenant du molybdène,l'un de ces trois,signé par "A", ne contient que de 2,4 % de molybdène, l'autre, signé par "K" est stabilisé à la fois par niobium. Le troisième,signé par "B" contient 4,5 % de molybdène. Il y a quatre alliages de chromo-nickel différents par leurs teneur en nickel, c'est à dire par la présence du stabilisant de titane. Dernièrement, on peut observer deux aciers de manganèse-azote appartenant à la série de teneurs différentes de manganèse.

Nous avons poli les échantillons bloqués dans une résine poliacrylic, puis on les a dégraissés par l'éther-diéthylique et par l'alcool absolu. La surface libre, ronde et polie des échantillons avait la superficie de 0,25 cm^2.

Nous avons fait les examens dans cinq solutions des acides différents. Chaque solution d'acide a 5 % (acide formique, acide acétique, acide oxalique, acide maléique, acide citrique), contenait encore 3 % de chlorure. On fait continuellement circuler les solutions pendant les épreuves.

RESULTATS

Sur les figures de 2 à 6 on présente les courbes des résultats particuliers de quelques alliages des aciers immergés dans des solutions d'acide formique, contenant aussi du chlorure.

La figure 2 présente la courbe de polarisation d'un alliage contenant 2,4 % de molybdène. Pour faire la comparaison on présente aussi la courbe expérimentale dans un milieu exempt de chlorure. On peut constater, que la couche se rompe après un temps de repassivation relativement court.

La figure 3 présente la courbe de polarisation des alliages contenant 4,5 % de molybdène. Dans ces cas la rupture des couches passives se retarde jusqu'aux potentiels positifs bien élevés. Le potentiel de rupture est plus positif que le potentiel d'oxydo-réduction du milieu (+220 mV).

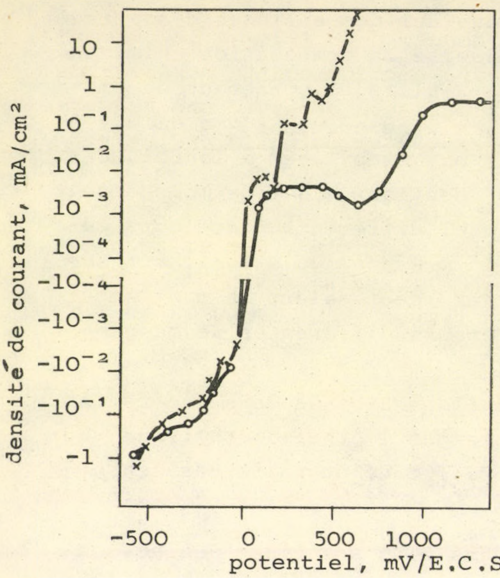


Fig. 2. L'alliage "A".

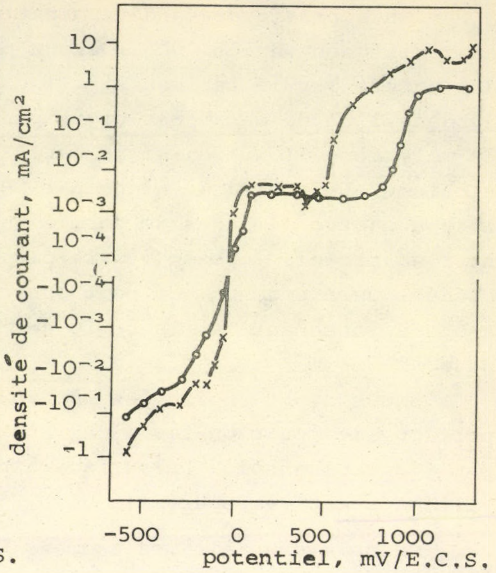


Fig. 3. L'alliage "B".

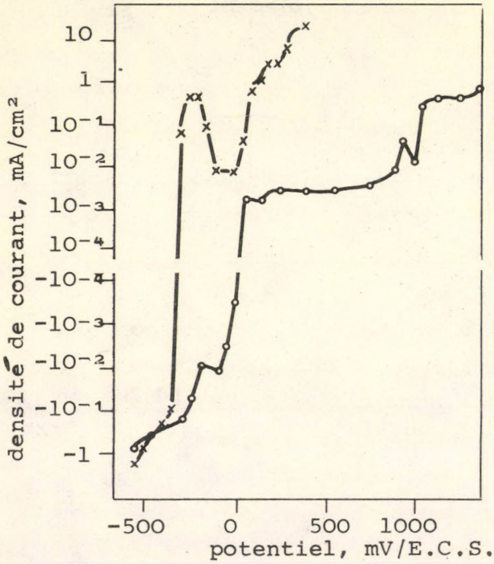


Fig. 4. L'alliage "E"

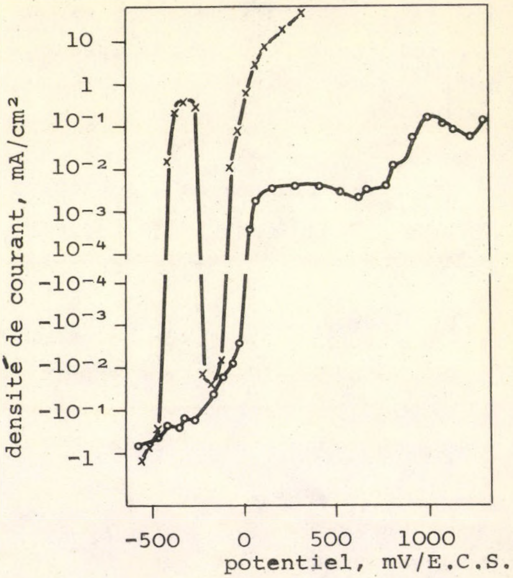


Fig. 5. L'alliage "G"

Les courbes de polarisation des alliages A B. E et G dans une solution d'acide formique à 5% (o), et l'acide formique à 5% + chlorure de sodium à 3% (x)

Sur la figure 4 on voit la courbe d'un alliage de chromo-nickel non stabilisé. On constate une section courte passive de courbe après un maximum de courant, puis on observe une augmentation brusque de la densité de courant a un potentiel relativement négatif.

La figure 5 présente une courbe de polarisation d'un acier de manganèse-azote faiblement allié au nickel. Cet alliage se comporte analogment comme le précédent, mais la couche se rompe à un potentiel encore plus négatif.

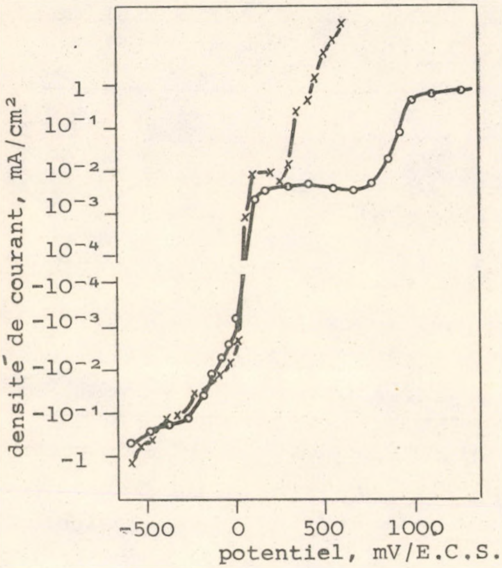


Fig.6. Les courbes de polarisation de l'alliage "K" dans une solution de l'acide formique à 5% (o), et l'acide formique à 5% + + chlorure de sodium à 3% (x)

On peut voir sur la figure 6 une courbe d'un alliage faiblement allié au molybdène, stabilisé par niobium. On peut constater de nouveau un domaine passif, large de 200 mV, puis la rupture de la couche qui arrive aux environs de la valeur du potentiel d'oxydo-réduction.

La figure 7 représente l'état de surface des échantillons d'alliage après un examen chronopotentiostatique effectué dans un milieu contenant de l'acide formique et du chlorure a un potentiel de + 100 mV E.C.S. . Dans ce milieu tous les alliages sont subis à une corrosion par piqûres exceptés les suivants: l'alliage fortement allié au molybdène signé par "B", l'alliage signé par "K" stabilisé, contenant du molybdène, et l'alliage signé par "C" stabilisé, contenant du chromo-nickel. Cependant le taux de corrosion par piqûres est bien différent. La corrosion par piqûres est bien répendue sur la surface des alliages mangenèses-azote, par contre sur la surface des autres alliages il n'y a que quelques piqûres.

Le résumé des résultats d'espériences executés dans une solution contenant de l'acide formique et du chlorure, selon les caractéristiques électrochimiques et l'appréciation visuelle , est présenté dans le tableau 2.

Tableau 2

Les caractéristiques des alliages dans une solution d'acide formique à 5 % contenant 3 % de chlorure de sodium

Le signe de l'alliage	E_C mV/E.C.S.	E_R mV/E.C.S.	I mA/cm^2	L'apparition des piqûres sur la surface
A	-221	+150	0,008	+
B	+171	+550	0,001	-
C	-177	+200	0,680	-
D	-381	0	0,840	+
E	-424	0	2,880	+
F	-447	-100	17,200	+
G	-464	- 50	44,400	+
H	-208	+200	0,280	+
K	-182	+300	0,018	-

On a considéré pour potentiel de rupture, la valeur de potentiel appartenant à 50 $\mu A/cm^2$ de densité de courant.

La densité de courant (I) est mesurée à la fin de 3o minutes de l'exament chronopotentiostatique.

Selon les donnés ainsi obtenues, il est évident que les alliages peu sensible ou non sensible à la corrosion par piqûres ont un potentiel stationnaire (E_C) relativement positif qui se forme tout de suite après l'immersion. La valeur du potentiel stationnaire de l'alliage signé par "B" prouve la passivation spontanée de l'alliage. Le potentiel stationnaire des alliages signés par "F" et "G", bien attaqués par la corrosion par piqures, à la valeur la plus négative.

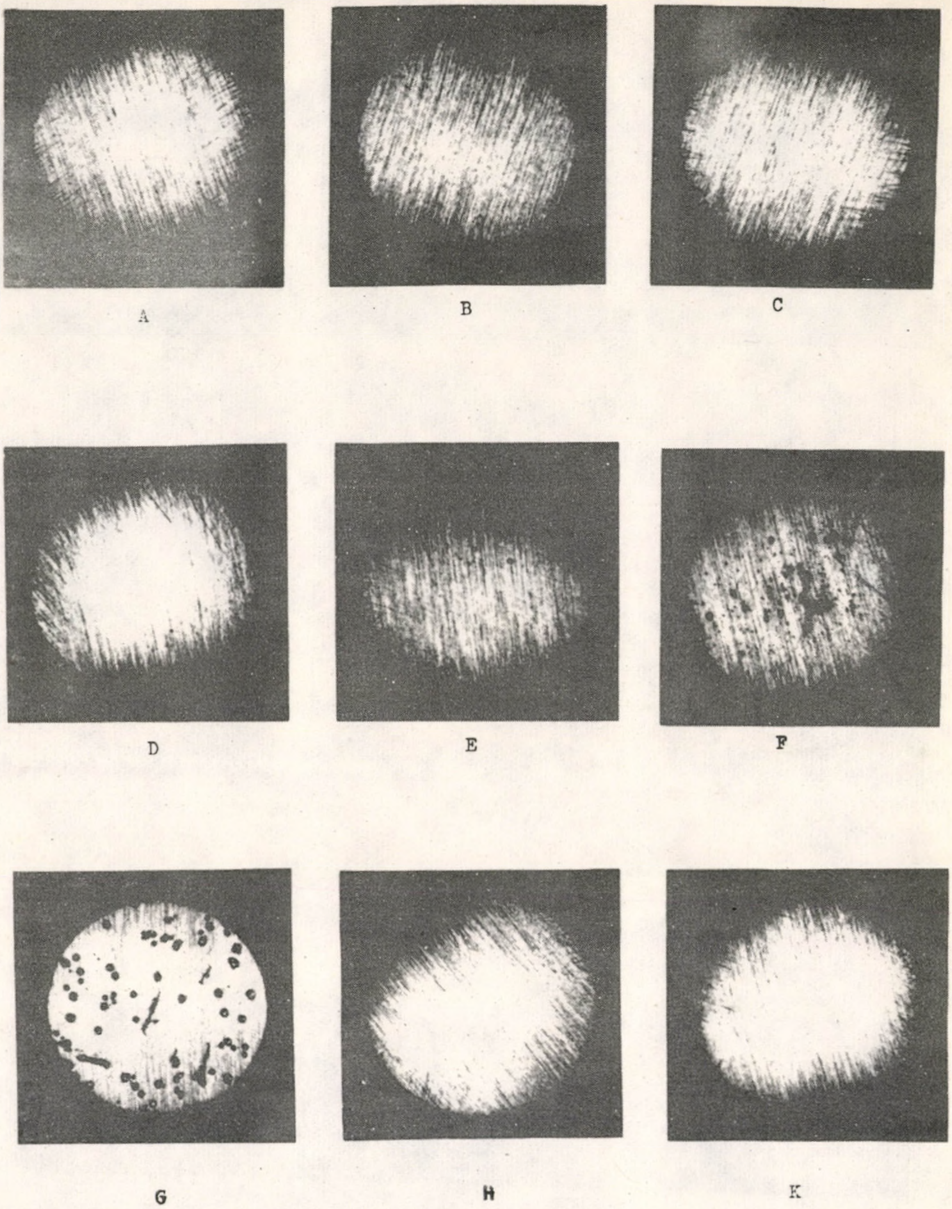


Fig.7. La surface des alliages après les examens chronopotentiostatiques exécutés dans une solution contenant de l'acide formique à 5 % + chlorure de sodium à 3 %.

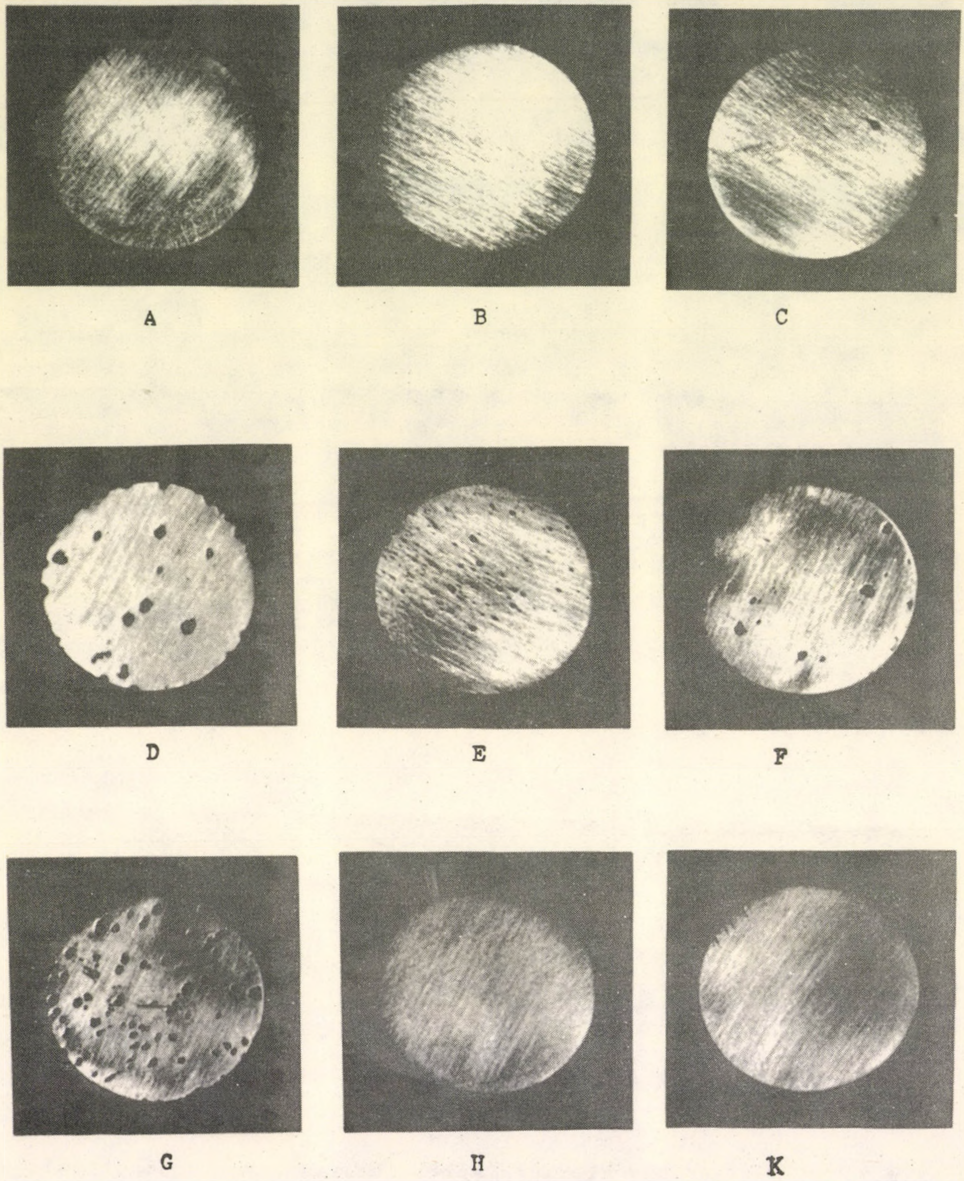


Fig.8. La surface des alliages après les examens chronopotentiostatiques exécutés dans une solution contenant de l'acide citrique à 5 % et chlorure de sodium à 3 %.

La valeur du potentiel de rupture (E_R) est relativement positive en cas des alliages résistants, et relativement negative en cas des alliages susceptible à la corrosion. Il y a un écarte de trois d'ordre de grandeur entre les densités de courant chronopotentiostatiques des alliages resistants et sensibles à la corrosion.

La figure 8 présente la surface d'une échantillon d'alliage, après avoir traité dans une solution, contenant d'acide citrique et de chlorure de sodium, et effectué un examen chronopotentiostatique. Quatre aciers se corrodaient intensivement, ce sont deux aciers de chromo-nickel sans stabilisation et les aciers de manganèse-azote. Sur les autres échantillons il n'y avait pas de corrosion.

Nous avons résumé dans la tableau 3 les caractéristiques formées dans un milieu d'acide citrique et de chlorure. Dans ce cas les alliages attaqués sont caractérisés par le potentiel de corrosion et de rupture bien négatif et par une grande valeur de densité du courant chronopotentiostatique.

Les observations sont pareilles en cas des échantillon immergés dans les autres milieu examinés.

Tableau 3

Les caractéristiques des alliages dans une solution contenant de 5 % d'acide citrique et de 3 % de chlorure de sodium

Le signe de l'alliage	E_C mV/E.C.S.	E_R mV/E.C.S.	I mA/cm^2	L'apparition des piqûres sur la surface
A	+195	+225	0,360	-
B	+222	+425	0,001	-
C	-142	+225	0,020	-
D	-477	- 25	1,120	+
E	-345	- 25	4,800	+
F	-450	-125	23,600	+
G	-350	- 75	48,800	+
H	+100	+225	0,002	-
K	-160	+325	0,232	-

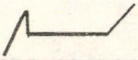
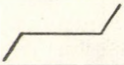
On voit le résumé des résultats d'investigation exécuté dans le tableau 4, qui sert à établir le rapport entre les caractéristiques électrochimiques et la tendance à la corrosion par piqûres.

En comparant les caractéristiques des alliages susceptibles et non susceptibles à la corrosion, on constate, que le potentiel de rupture des alliages susceptibles à la corrosion se déplace vers les potentiels relativement négatifs. Cette valeur est relativement positive aux alliages résistants à la corrosion.

Le potentiel stationnaire est aussi bien negatif,(environ -400 mV/E.C.S.), dans les alliages susceptibles à la corrosion.

Tableau 4

Le rapport entre les caractéristiques électrochimiques et la tendance à la corrosion par piqûres

Caractéristiques électrochimiques	Alliage susceptible à la corrosion par piqûres	Alliage relativement resistant à la corrosion
Potentiel de rupture	$- \longleftarrow E_R$	$E_R \longrightarrow +$
Potentiel stationnaire	$- \longleftarrow E_C$	$E_C \longrightarrow +$
Densité de courant chrono-potentiostatique	$i > 1$ mA	$i \longrightarrow 0$
Forme du courbe de polarisation		

En faisant la polarisation à un potentiel constant, par exemple à 100 mV positif, la densité de courant atteint la valeur de 1 à 10 mA/cm^2 aux alliages susceptibles à la corrosion. La densité de courant est très petite dans les alliages résistants à la corrosion, ces valeurs ne dépassent pas quelques µA.

Sur la courbe de polarisation d'un alliage susceptible à la corrosion on aperçoit un maximum de courant, qui est caractéristique à la solution active, dans un milieu investigé, et qui ne se montre pas aux alliages résistants à la corrosion.

CONCLUSION

Selon l'appréciation au-dessus décrite et l'analyse de tous les résultats - malgré les relations qualitatives et générales - on constate, que la discussion d'une caractéristique isolée n'est pas suffisante dans l'évaluation de la tendance à la corrosion. Il est nécessaire évaluer ensemble les caractéristiques reçues des courbes de polarisation anodique et des mesurements exécutés au potentiel constant pour qu'on puisse qualifier les alliages selon la tendance à la corrosion par piqûres. Mais le potentiel de rupture se montre exeptionnel, s'il a une valeur plus haute que le "redox" potentiel car dans ce cas la corrosion par piqûres est exclue.

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РЕЗЮМЕ

Автором была исследована склонность разных аустенитовых стальных сплавов к точечной коррозии, применив кратковременный потенциостатовый и хронопотенциостатовый метод в растворах содержащих органические кислоты и соприкасающихся с воздухом. Изучались значения отдельных электрохимических показателей при сплавах склонных и несклонных к точечной коррозии. Качественные соотношения общего действия были обнаружены между свойствами сплавов и их показателями. На основе этого во всех случаях можно осуществить относительное сравнение свойств различных сплавов по точечной коррозии. Для квалификации определенного сплава, однако, необходимо точно определить величины вообще нескольких показателей. Помимо определения потенциала прелома получается полезная информация на основе хронопотенциостатового испытания, выполненного при подходящем потенциале.

CORRIGENDUM

In HJIC Vol. 2. Suppl. 2. the title of G. Kováts' article was published wrongly. The correct title is:
"Problems of Securing Monomers for the Production of 1,4 - cis - - polyisoprene Caoutchouk".

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