30TH MEETING

HELD AT

CENTRE FOR HIGH TECHNOLOGY,
SCOPE COMPLEX, NEW DELHI

ON

AUGUST 25, 1994

No.J-13012/1/92-Gen.
Government of India
Ministry of Petroleum & Natural Gas

.....

New Delhi, the 14th September, 1994.

To

1. Members of the Scientific Advisory Committee on Hydrocarbons of the Ministry of Petroleum & Natural Gas (By name)

2. Chief Executives of Oil Companies

Subject:- Meeting of the Scientific Advisory Committee on Hydrocarbons of the Ministry of Petroleum & Natural Gas - Circulation of the Minutes.

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Sir,

I am directed to forward herewith a copy of the minutes of meeting of the Scientific Advisory Committee on Hydrocarbons of this Ministry, held in New Delhi on 25th August, 1994, for information and necessary action.

Yours faithfully,

(K.C. Katoch)
Under Secretary to the Govt. of India.
Tel No.384376

Copy to :-

1. Prof.M.M. Sharma, Professor of Chemical Engineering and Director of Chemical Technology, University of Bombay, Matunga, Bombay-400 019.

Copy also to:-

1. JS(E)/JS(R)/JS(M)/Adv.(E)/OSD(R)-(Shri K.P. Sahi)/DS(CC)
2. ED,CHT, NEW DELHI.
3. FA&CAO, OIDB, NEW DELHI
4. PS to Secretary(P&NG)

(K.C. Katoch)
Under Secretary to the Govt. of India.

Minutes of the 30th meeting of Scientific Advisory Committee(SAC) of the Ministry of Petroleum & Natural Gas held at SCOPE Complex, New Delhi on 25th August, 1994

List of participants is attached.

Shri Christy Fernandez, JS(C&A) of Ministry of Petroleum & Natural Gas extended a warm welcome to Prof.M.M.Sharma as the new Chairman of the SAC and other distinguished members and invitees. He desired that the Committee, apart from deliberating on various developmental issues, need to work on the future strategies to be adopted by the Govt. in the petroleum sector. This has become very relevant in view of the changing scenario brought about by the liberalisation of the economy and the resultant globalisation. SAC may also deal with frontier areas of technology and advise the Govt. suitably to enable it to develop policy guidelines. Shri Fernandez also emphasised that to have fruitful deliberations and meaningful interaction, all members of the Committee should be present in the meetings and requested Prof.Sharma to look into the ways and means to ensure larger attendance. He expressed his confidence that with Prof. Sharma at the helm of affairs as Chairman, the Committee would prove more effective to meet the objectives outlined in the terms of reference for the Committee.

Thanking the Ministry for the confidence reposed in him in nominating him as Chairman of the Committee, Prof.Sharma said that this SAC has been doing a very good job and is often cited as a model Committee in various forums. He, however, assured Shri Fernandez that the Committee will keep in mind the expectations of the Ministry from the Committee in making clear cut recommendations in terms of basic policies. Prof.Sharma also mentioned briefly about the important issues which need to be addressed by the industry, namely, the need to respect relevant hydrocarbons as feedstock first and fuel later with a view to exploit the opportunities of producing value added products. Also, there is an urgent need to look into the quality aspects of

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petroleum products now being produced in our country and find ways and means to upgrade them suitably to be competitive in the liberalised marketing scenario.

With regard to the comment about non-participation of the members of the SAC in its meeting, Prof.Sharma felt that those who find it difficult to attend the meetings could volunteer to quit from the membership of the Committee. He also said that heavy responsibility lies on the Committee as everyone watches the functioning of the petroleum sector keenly since all individuals are affected by this sector in some way or the other. It is, therefore, necessary that the Committee members attach due importance to the responsibility given to them while the Ministry nominated them to the Committee.

Prof.Sharma recalled the services of late Shri Lovraj Kumar and wanted to put on record his exemplary leadership in directing and guiding the functioning of this Scientific Advisory Committee. All participants stood in silence for a minute as a mark of respect to the departed soul.

30.0 Review of Action Points of the 28th meeting held on 3-4 Nov.1993

30.1 Item-28.2 - EIL's note on the extraction pilot plant facilities at HPCL(B), MRL and EIL(R&D) will be taken up for discussion later.

30.2 Item-28.4 - The Chairman advised that the development of process for LPG sweetening should also consider the removal of carbonyl sulphide, as the same subsequently leads to the formation of hydrogen sulphide in LPG, due to hydrolysis.

30.3 Item 28.5 - Etherification of FCC gasoline

IIP will submit a revised proposal on 'Etherification of gasoline' considering the EIL's note also in this regard. Etherification of gas oil fraction can be considered later. IIP & EIL are also to

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consider various options like alkylation and isomerisation of suitable naphtha fractions, considering the anticipated changes in MS specifications with respect to permissible aromatics and benzene in MS. A note in this regard will be prepared by EIL and IIP and submitted to SAC.

30.4 Item 28.7 - IIP's proposal on Microbial desludging of crude oil tanks

IOC agreed to provide necessary facilities to IIP at Gujarat refinery for testing their technique in a small tank before it can be used in bigger crude oil tanks. IIP should develop a proposal in consultation with IOCL and present in the next SAC meeting.

In this connection, OSD(R) informed that Secretary MOEF has written to Secretary P&NG enclosing a proposal of NEERI on bio-desludging of tank sludge and have offered to demonstrate their process. It was decided that IIP will co-ordinate with NEERI and one more refinery site will be selected for demonstration of the technology of NEERI.

30.5 Item 28.8 - Supercritical solvent recovery in solvent deasphalting process

IIP and EIL will prepare a paper on the subject incorporating relevant factors like the extent of revamping required, order of magnitude cost and implications thereof and the feasibility of adoption in the units of IOC(Haldia), MRL and HPCL(B). The potential users of this process, namely, IOC, MRL and HPCL will also be involved in developing this process by IIP/ EIL. This matter will be taken up for discussion in the meeting after the next.

30.6 Item-28.24 - Rubberised bitumen as road pavement material

The Chairman indicated that the tendency of natural rubber to degrade fast needs to be considered while developing the rubberised bitumen. CRL will take note of this.

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30.7 Item-29.22 - Short Path Distillation Unit

RRL, Jorhat alongwith IOC (Digboi) will work out the economics of the proposal considering factors such as:

i) Pilot plant of adequate capacity to be located at Digboi Refinery.

ii) The pilot plant can also be used for testing of other Indian crudes to examine the feasibility of producing value added products from the bottom of the barrel.

iii) This facility will have the status of National Testing Centre for this purpose.

iv) This facility should be considered for the manufacture of microcrystalline wax in addition to bitumen and the return on investments to be worked out accordingly, considering market potential of MCW within the country and outside etc.

Additionally, competitive technology like 'Deep Cut Distillation' also needs to be studied and compared.

30.8 The Chairman stressed that we should maximise recovery of valuable olefins of C_3 and C_4 fractions from cracker streams, as petrochemical feedstocks. These Hydrocarbon streams of refineries should be treated primarily as feedstocks for petrochemicals and not as fuels.

30.9 The following new proposals will be taken up for discussion during the next meeting.

i) Technology development for the production of high quality microcrystalline waxes using short path distillation technology - RRL, Jorhat.

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ii) Development of CFPP/PPD additives for diesel fuels - RRL, Jorhat.

iii) Production of microbial biosurfactants useful in petroleum industry - RRL, Jorhat.

iv) Studies on the effect of soaker geometrics and internals on visbreaking process.

30 copies each of the proposals need to be sent by the concerned organisations to CHT by 15th September, 1994 for forwarding the same to SAC members for their perusal and comments.

30.10 The next meeting will be held at BPCL refinery, Bombay on 6th October, 1994. The meeting will start at 9.00 hrs and left over agenda items of this meeting and the above noted new proposals will be taken up for discussion.

ANNEXURE

30th meeting of SAC held at Scope Complex,New Delhi on August 25,1994 - List of participants.

I. Chairman : Prof.M.M.Sharma

II. Members

* Shri K.P.Shahi,OSD (R)
* Shri K.Vasudeva,IIT,Delhi
* Dr.R.S.Venkataraman,EIL,Delhi
* Dr.S.Varadarajan,Ex-Consultant,Planning Commission
* Shri J.K.Das,PCRA
* Dr.T.S.R.Prasada Rao,IIP,Dehradun
* Dr.A.C.Ghosh,RRL,Jorhat

III. MINISTRY

* Shri Christy Fernandez
* Shri K.C.Katoch

IV. Invitees

HPCL

* Shri M.Sreekanth

EIL

* Shri S.C.Gupta
* Dr.S.J.Chopra
* Dr.B.S.Gill
* Dr.S.Banik

CRL

* Shri P.M.Mani
* Dr.M.A.Siddiqui

OISD

* Shri J.N.Mathur
* Shri M.Srivastava

MRL

* Shri A.Varadarajan

BRPL

* Shri J.M.B. Baruah
* Shri R.M.Hazarika□ □

BPCL

* Shri S.Viswanathan

IOC(R&P)

* Shri G.R.Sampath
* Shri Sanjiv Kumar

IOC(R&D)

* Dr.A.K.Bhatnagar
* Shri A.M.Uplenchwar
* Dr.S.Ghosh
* Dr.S.P.Srivastava

LIL

* Shri M.G.Banerjee
* Dr.A.S.Sarma

IBP

* Shri R.K.Narang

IIP

* Shri O.N.Anand
* Dr.B.S.Rawat
* Shri R.P.Malhotra
* Dr.Himmat Singh
* Dr.K.S.Jauri
* Shri S.Singhal
* Dr.K.K.Bhattacharrya
* Shri G.S.Dang

Balmer Lawrie

* Dr.P.R.Nambiar

RRL - Jorhat

* Dr.A.A.Rigvi
* Dr.I.Suryanarayana
* Dr.K.V.Rao

CHT

* Shri A.M.Prasad
* Major S.C.Agarwal
* Shri S.Venkatraman
* Shri M.Kannan
* Shri B.J.Talukdar
* Shri Sanjiv Singh

Status of Action Taken pertaining to 29th meeting of Scientific Advisory Committee

Sl No	MOM Item No	ITEM	STATUS
1	29,3	Utilisation of Jatropha curcas oil as diesel fuel - Actions subsequent to discussion with Deptt. of Wasteland Development.	IIP had presented their project proposal to Dept. of Waste Land Development. They have submitted a pre- feasibility report for the manufacture of diesel component from Jatropha curcus oil for the consideration of SAC. To be taken up in the next meeting of SAC.
2	29,4	Re-refining of used lube oils: IIP,EIL & IOC(R&D) are to recommend the best eco-friendly technology.	IIP & IOC (R&D) have prepared a joint note wherein they have observed that the best option would be to adopt a two stage process : vac. distillation of dehydrated waste oil followed by hydrotreating of distilled stocks. They are prepared to submit a project proposal for the development of a eco-friendly technology if approved in principle by SAC.
3	29,5	Catalyst and process development for hydrogenation of coker distillate.	IOCL is not keen. BRPL has shown interest.IIP is pursuing with BRPL.
4	29,7	Identification of Research Institute for R&D work related to FCC catalyst additives.	Letters were addressed to IIP, RRL Trivandram, IIT Madras, NCL Pune & IICT Hyd. Response received from all except RRL Tvm. CHT will finalise the program of work in consultation with these institutes and R&D centres of oil companies.
5	29,10	Instrumentation & testing facilities for yield and energy optimisation in refineries.	Refineries have been carrying out yield & optimisation studies with the help of consultants identified by them. These consultants have identified the various hardware & software requirements for refineries to carry out such studies by themselves. Therefore EIL had discontinued this exercise.

Sl No	MOM Item No	ITEM	STATUS
6	29,12	Progress on the proposal of IIT, Kanpur on Advanced Control	Approval to be obtained from the Executive Committee of CHT.
7	29,14	Development of mathematical modelling groups in refineries.	IIT, Bombay had designed two training programmes to train refinery personnel. The software required for this purpose is to be selected by IIT, Bombay in consultation with EIL (R&D). This will be followed by preparation & submission of a firm proposal by IIT, bombay.
8	29,16	R&D needs related to safety techniques	OISD has funded a project to EIL on 'Water spray nozzles - Performance testing for industrial safety'.
9	29,17	Status on development of process package for reformer	Development of process design capability for SR type CRU has been completed by EIL ∝ IIP.
10	29,20	Desalination of sea water for cooling purpose	Permeate recovery was very low with CSMCRI membrane. MRL to follow up.
11	29,24	Re-refining of used lube oils - Trial run of Balmer Lawrie's pilot plant.	Report received and sent to IIP, EIL(R&D) & IOCL (R&D) for comments. The comments received from IIP & IOC (R&D) is enclosed.
12	29,25	Oil Industry Pipelines - Proposal for developing intelligent pig for health monitoring	IOC (R&D) is finalising the terms & conditions with BARC for developing the pig indigenously.

as a building unit for fine chemicals? For example, can we use a diene and carbon dioxide to form lactones? It is not that we want to contribute to or avoid the Greenhouse effect, but just as we used carbon monoxide as a building unit, why don't we use carbon dioxide in the future?

Bader: Assuming the model you just presented, in which the electronic density of the metal center varies, are there any examples in homogeneous catalysis, like titanium chemistry where one can influence the Lewis acidity by organic ligands? It is easier for me to think of fine tuning of such a catalyst than of a solid oxide.

Tanabe: In the homogeneous case, the acidity depends on the nature of the ligand. Recently we measured the acidity of the metal complex and ruthenium and rhodium showed a very high acidity.

Maxwell: With reference to the sulphate/zirconia catalyst, would you not expect under the reducing conditions you mentioned that the sulphate would be reduced?

Tanabe: If the reaction temperature is higher than 200 degrees; at a lower reaction temperature, a super acid will not be reduced even with hydrogen. Therefore it is very important to avoid reaction temperatures above 200 degrees under reducing conditions.

ELSEVIER

Applied Catalysis A: General 113 (1994) 153–173

applied catalysis A

The pivotal role of catalysis in energy related environmental technology

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The Netherlands

1. Recent trends

This overview will cover recent developments in environmentally related heterogeneous catalysis with respect to the energy industry and will include oil refining, natural gas conversion and emission control technologies. In addition, future energy trends and the generic areas of catalysis that will be of importance tomorrow in the energy industry will be discussed.

Worldwide significant continued growth is expected in terms of energy consumption and fossil fuels are expected to remain very important well into the foreseeable future. There is a marked difference in terms of energy growth between the developed countries, Europe, the US and the developing countries (Fig. 1). For example, in the next 10–15 years some 30 new refineries are expected to be built in the Far East, China and India.

In general, proven oil reserves are slowly eroding while gas reserves continue to grow quite rapidly. As oil becomes scarcer, the quality of crude oil as is reflected, for example, in the hydrogen content tends to decrease (Fig. 2). In terms of product trends it is expected that factors such as requirements for reduced emissions, a shift towards middle distillates and improved combustion performance will likely require that the hydrogen content of transportation fuels will on average increase. These trends will lead to a 'hydrogen gap' which will require more hydroprocessing in refineries, with a concomitant need to produce more hydrogen in the future.

Environmental legislation will continue to strive for lower emission levels, particularly for sulphur dioxide, NO_x, and volatile organic compounds (VOC's). In oil refining during the last 15 years, for example, within Western Europe, there has been a very significant reduction in sulphur emissions, in terms of sulphur both in the refinery gas streams and in transportation fuel products (Fig. 3).

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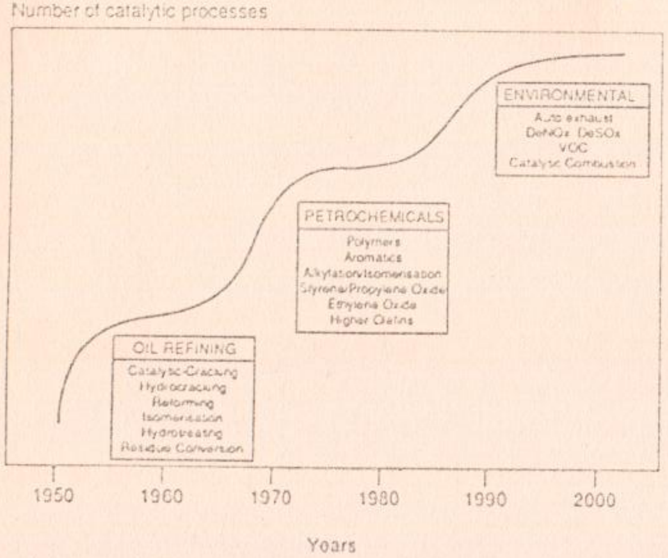


Fig. 5. Quantum developments in the industrial application of heterogeneous catalysis.

1950's, there was a major thrust in applying catalysis to oil refining processes. Important catalytic process technologies were developed such as catalytic cracking, hydrocracking and catalytic reforming. These catalytic technologies are still the cornerstones of a modern refinery for achieving heavy oil conversion and fuel quality upgrading. Catalyst developments related to these processes has resulted in continued incremental improvement in these process technologies.

In the 1970–1880's, there was a thrust towards the application of catalysis in petrochemicals, particularly for the production of the bulk polymer intermediates. Some innovative new technologies were developed such as the Shell SMPO process in which styrene monomer and propylene oxide are co-produced making use of a titanium based heterogeneous oxidation catalyst. Also, for example, during this period Mobil developed and commercialized a number of processes for the isomerization, disproportionation and alkylation of aromatics utilizing their novel shape selective synthetic zeolite ZSM-5 as a catalyst.

The next major thrust for the 1990's in heterogeneous catalysis technology is already emerging in the area of environmental applications.

The first generation of environmental related catalytic technologies (Fig. 6) were, in fact, developed in the early 1960's–1970's, such as hydrotreating processes to remove heteroatoms such as sulphur and nitrogen from crude oil and intermediate products. The catalyst systems developed were based on supported mixed sulphides systems (e.g. Co/Mo and Ni/Mo) which are resistant to poisoning by sulphur. The treatment of the H_2S produced from hydroprocessing made use of catalytic Claus technology to convert H_2S into elemental sulphur.

In addition, the advent of lead-free gasoline which required a hydrocarbon based octane replacement stimulated the development of novel catalytic processes such

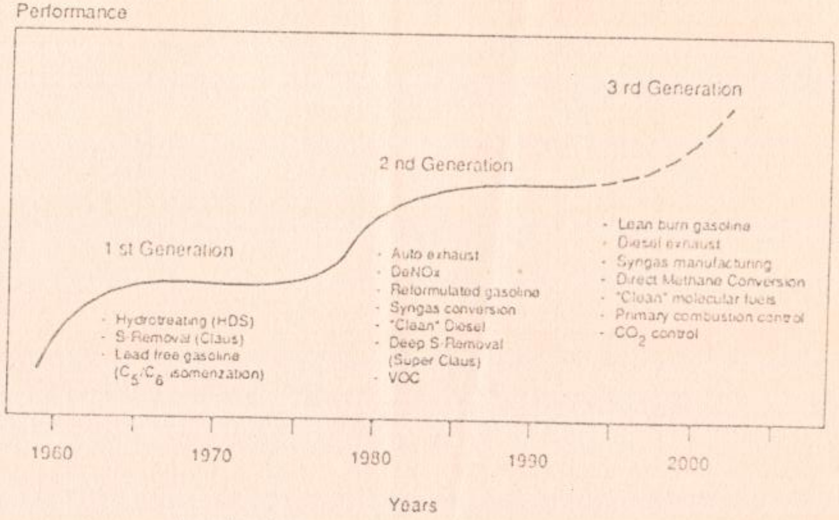


Fig. 6. Developments in catalytic environmental technologies.

as the isomerization of C_5 and C_6 alkanes which employs a zeolite (mordenite) based solid acid catalyst. In the early 1980's and 1990's, a second generation of environmentally driven catalytic processes have emerged. These include, automobile exhaust control, NO_x, SO_x and VOC removal processes, reformulated gasoline and syngas conversion processes. For example, the second generation Claus process (Super Claus) achieves efficient sulphur removal using a more sophisticated catalyst system.

2. Environmentally driven catalytic refinery technologies

In a modern oil refinery the aim is to maximize the yield of high quality liquid transportation fuels and minimize by-products such as heavy residue and light gases which represent a downgrading relative to the cost of the crude oil. There is an increasing emphasis not only on upgrading but also on the environmental aspects with respect to oil refinery products. This has led to a wave of environmentally driven new and improved catalytic refining process technology.

The expected trends in transportation fuel composition are given in Table 1. While gasoline octane requirements will remain quite high, lead, sulphur and benzene levels will all significantly decrease. Sulphur levels are legislated at below 100 ppm in the US, but some countries are considering even lower levels. The isoalkane and oxygenate contents will increase to provide octane quality (Table 2) and the latter component has been legislated in the US for reformulated gasoline as part of the Clean Air Act primarily to reduce auto exhaust CO emissions.

For diesel the sulphur and aromatic levels will be decreased although the latter is under debate and legislation will likely differ significantly between various

Table 1
Expected trends in transportation fuel composition

Fuel	Characteristic	Change	Comment
Gasoline	Lead content	↓	Reduced lead emissions; Prerequisite for use of exhaust catalysts
	Benzene content	↓	Reduced toxic benzene emissions
	Sulphur content	↓	Reduced sulphur inhibition of exhaust catalyst activity and the risk of H$_2$S emission
	Vapour pressure	↓	Reduced evaporative hydrocarbon emissions
	Isoalkanes content	↑	Increase octane quality
	Oxygenates content	↑	Reduced exhaust emissions of CO but increased those of aldehydes (and nitrogen oxides)
Diesel	Sulphur content	↓	Reduced exhaust particulate emissions
	Aromatics content	↓	Increased cetane number
	Volatility	↑	Reduced exhaust emissions

countries. In general, there will be a trend towards higher cetane numbers which will also be reflected in a lower aromatics content of diesel fuel. The relationship between aromatics levels and diesel emissions has been studied extensively in recent years. Current data suggest that the density of the fuel is the prime parameter affecting emissions with the aromatic content only having an indirect effect.

In the past boiling point range and combustion performance were the prime measures of fuel quality; however, in the future molecular composition will be of increasing importance. For example, there has recently been a strong trend towards the incorporation of oxygenates primarily in the form of methyl tertiary butyl ether (MTBE) into gasoline, particularly in the US. The driving force for this development is both emissions control and attractive octane properties (Table 2). As a result the worldwide production of MTBE has increased dramatically in recent years (Fig. 7). The size of the global gasoline pool is so large, that the incorporation of even 10–15% of an ether has a huge impact in terms of demand. This shift towards the inclusion of MTBE into gasoline has led to a shortage of iso-butene which is a precursor along with methanol in the production of MTBE (Fig. 8).

One route to increase iso-butene production is by the isomerization of n-butene which is available from steam crackers, catalytic crackers or by dehydrogenation

Table 2
Octane properties of some gasoline components

	RON	MON	Volatility (RVP) (psi)
MTBE	118	100	8–10
ETBE	118	102	3–5
TAME	111	98	1.5
iC$_5$–C$_6$	75–102	75–102	6–27
Alkylate	92–97	90–94	3.5–4.5

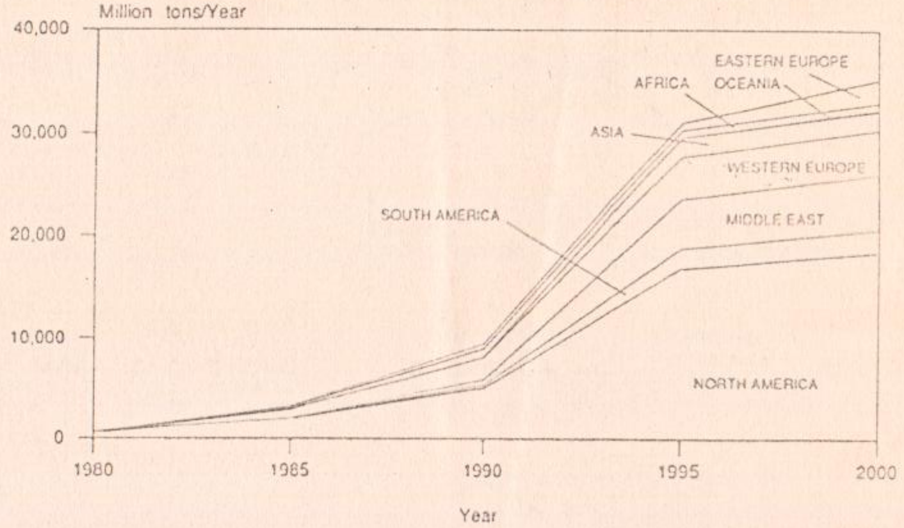


Fig. 7. Worldwide growth in MTBE production.

of iso-butane (Fig. 9). However, until recently the former route to iso-butene has not been very attractive due to the lack of a selective catalyst to effect the alkene isomerization reaction. Research was initiated a few years ago within Shell in this field and after screening a whole range of catalysts it was discovered that shape selectivity was a critical catalyst characteristic to steer this reaction towards the desired alkene isomerization rather than undesired dimerization [1].

Medium pore zeolites were found to exhibit shape selective behaviour for this reaction and, in particular, ferrierite, a uni-dimensional ten-membered ring zeolite (Fig. 10), was shown to have significant performance advantages over other catalysts. Mechanistic studies (Fig. 11) indicate that this reaction likely goes through a dimerization step to form a C_8 intermediate, which then undergoes isomerization followed by selective cracking of this C_8 intermediate to produce two molecules of iso-butene. Molecular modelling and computational studies provided insight indicating that relatively high diffusional resistance of this C_8 intermediate is an important catalyst characteristic for optimal shape selective control of this reaction.

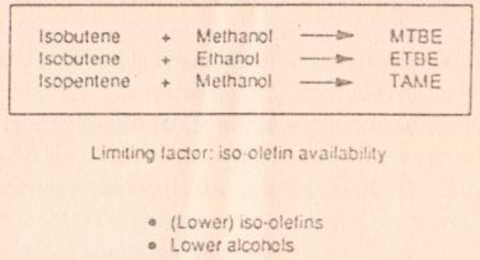


Fig. 8. Routes to ether manufacturing.

For example, in residue FCC many catalyst companies have developed metal traps which retard vanadium (a metal impurity in residue) migration to the zeolite Y component of the catalyst where it destroys the structure resulting in a marked loss in performance [3]. In addition matrices with larger pore structures than the zeolite Y component have been developed which facilitate pre-cracking of the larger molecular weight residue components which can then further crack more selectively to gasoline over the zeolite. There has also been quite some growth in the application of additives to the FCC process to assist in the control of SO$_x$ emissions and CO combustion in the regenerator. In addition, more recently shape selective zeolites such as ZSM-5 have been employed [4] to enhance the alkenes make in the FCC unit (Fig. 12). This trend has been stimulated by the shift towards ethers in gasoline since ZSM-5 addition to the FCC unit can provide an attractive means of increasing iso-butene (MTBE precursor) yields in the refinery.

In residue hydroprocessing the trend towards multi-bed and multi-reactor systems using tailored catalyst systems is also continuing to be further developed with increasing capabilities of handling heavy feedstocks [5]. In general, the front bed catalyst systems are designed for maximum metals (Ni, V and Fe) removal capacity in order to protect the downstream catalyst systems from metals poisoning. However, recent developments based on wide pore alumina supports have led to metals removal catalysts which also have an increasing capability to remove sulphur (HDS) and even some nitrogen (HDN). Traditionally the middle bed catalyst systems employ powerful HDS and HDN catalysts to reduce sulphur and nitrogen to low levels and hydrogenate aromatic structures.

Perhaps the most significant development in residue hydroprocessing in recent years has been the development of so-called bottom bed catalysts which enhance hydrocracking and increase the yield of light products. In fact, even zeolite based catalysts which have traditionally only been employed in distillate hydrocracking are now being developed and applied in the bottom bed of residue hydroprocessing units.

Developments have also continued in the reactor technology employed in residue hydroprocessing which include multi-catalyst fixed bed reactors with counter current hydrogen gas flow, ebullating beds and moving beds. Catalyst systems also need to be tailored, including the geometrical shape to match the particular reactor technology.

Other developments in hydroprocessing which have been driven by environmental factors include aromatics hydrogenation technology for diesel fuels. As previously discussed in selected areas of the world such as Sweden and California legislation has been introduced to reduce both sulphur and the aromatics contents of diesel fuels. Some new technology has been developed in Shell [6], for example, whereby very deep (< 10% vol aromatics) hydrogenation can be achieved. This process involves two stages (Fig. 13) whereby the first stage employs a conventional hydrotreating catalyst (Ni/Mo/alumina) to reduce nitrogen and sulphur levels. The heteroatom containing gases (i.e. H_2S and NH_3) are removed by an interstage flashing step and the liquid first stage product is further processed in a second stage. The new aspect of the process is the development of a novel zeolite catalyst for the second stage which is a powerful aromatics hydrogenation catalyst with a high tolerance to sulphur and nitrogen impurities which are carried over from the first stage. This process is now successfully producing low aromatics diesel products (e.g. so-called city diesel, < 10% aromatics and < 5 ppm sulphur) in a refinery in Sweden.

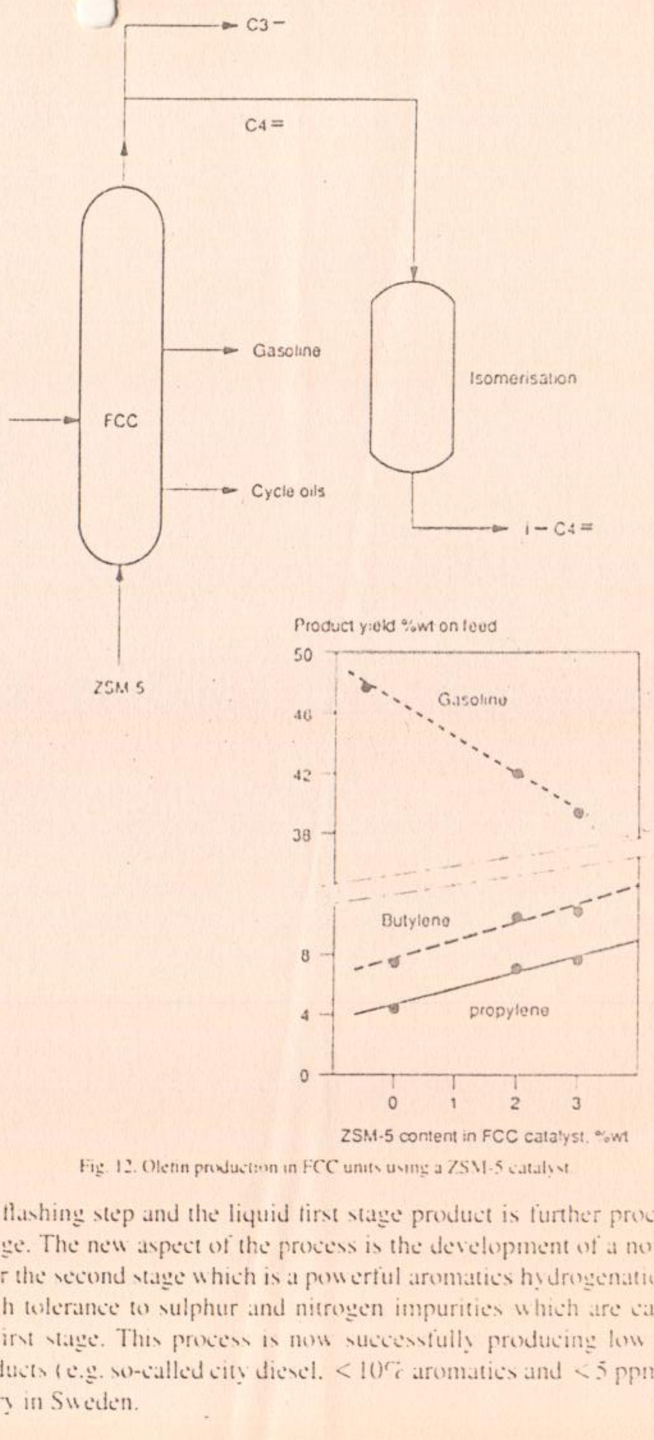


Fig. 12. Olefin production in FCC units using a ZSM-5 catalyst.

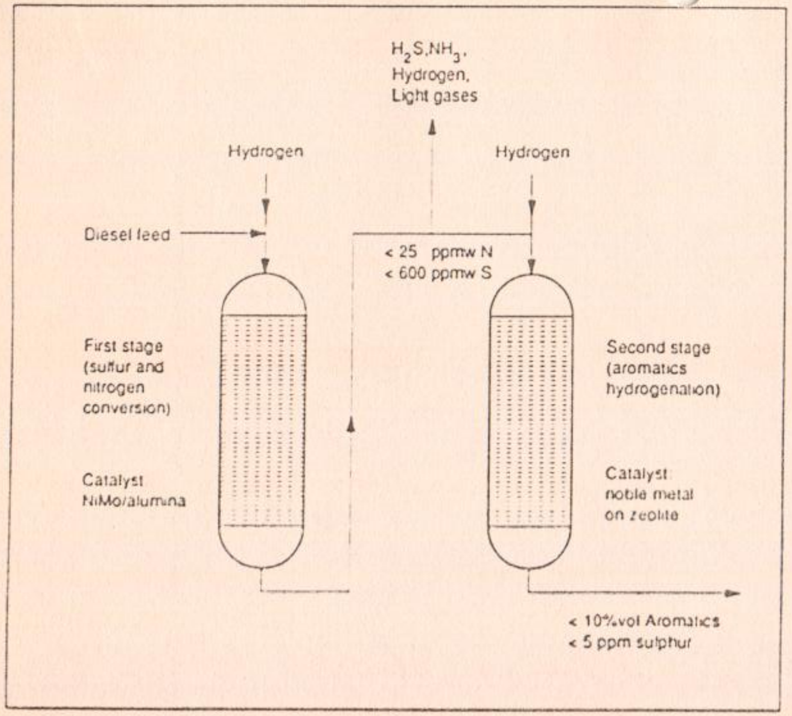


Fig. 13. The shell two stage hydrogenation process for low aromatics diesel fuels.

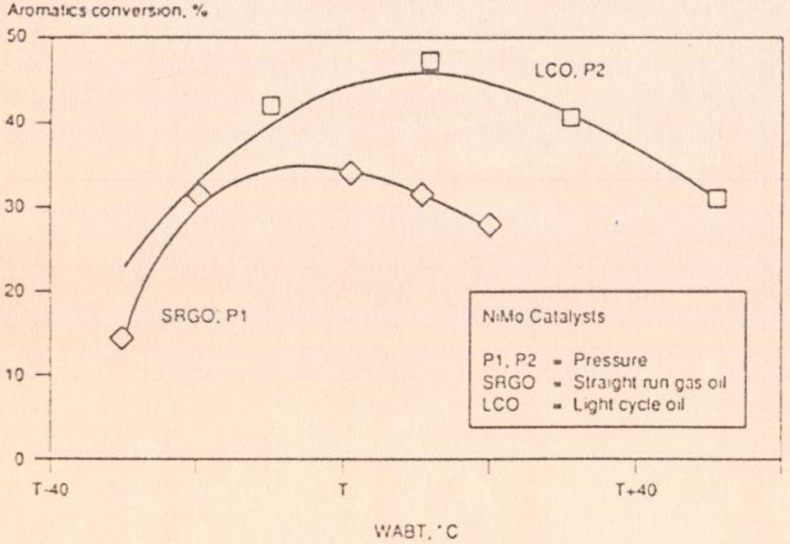


Fig. 14. Temperature limitations for aromatics conversion in conventional hydrotreating processes.

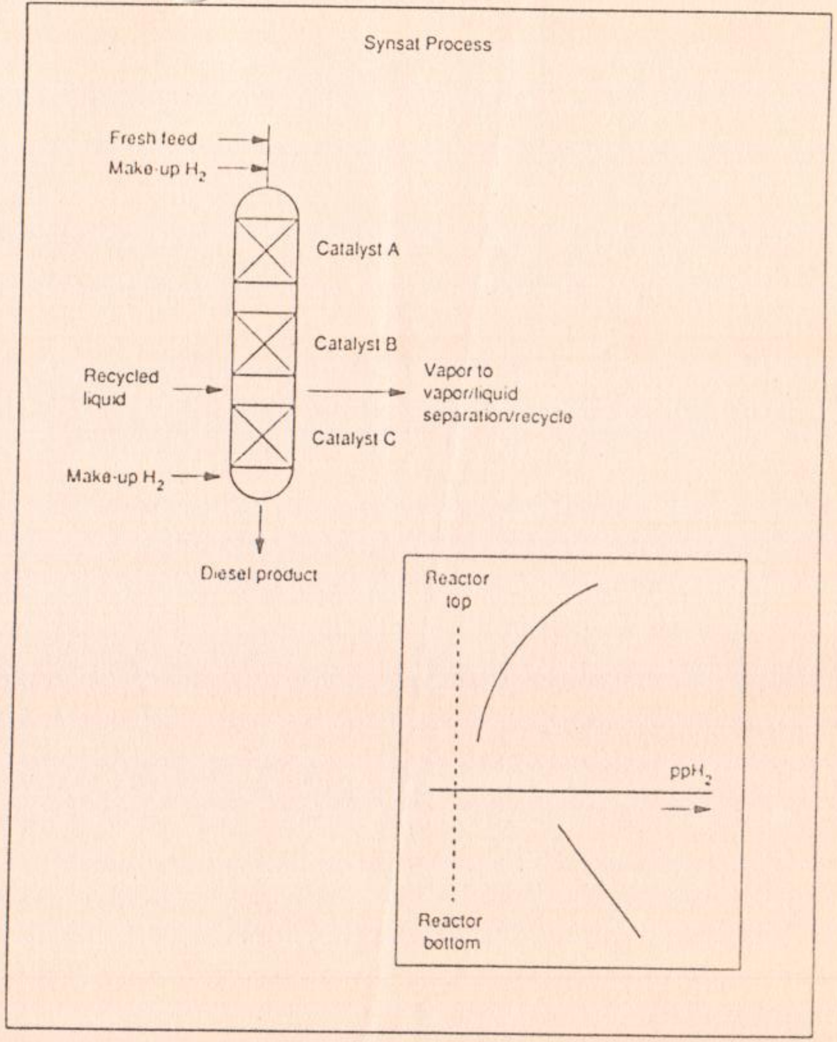


Fig. 15. The Synsat hydrotreating process for deep hydrotreating.

Also in the field of conventional hydrotreating there are some new developments again driven by legislation primarily related to reducing sulphur levels and aromatics in diesel products. Refiners have been operating hydrotreating reactors at maximum severity but as the operating temperatures continue to increase a limit is reached in terms of sulphur removal and particularly aromatics conversion (Fig. 14). An interesting new approach to improve the performance of hydrotreaters has been the development of multiple bed reactor systems. For example, the so-called Synsat process (see Fig. 15) employs multiple catalyst beds in which the bottom bed can be operated counter-current [7]. This enables a relatively high hydrogen partial pressure to be achieved in this part of the reactor and a resultant improved hydrotreating performance. In addition, more powerful noble metal based hydrotreating catalyst systems can now be employed in such a bottom bed without severe deactivation.

3. Natural gas conversion developments

Another area of fuels development in which catalytic technology is playing an important role is natural gas conversion. These developments are driven by the desire to exploit natural gas which is in remote locations. Natural gas as a feedstock has the advantage of having a high hydrogen content, which is particularly advantageous for the production of low aromatics containing middle distillate fuels. A close match between feed and product hydrogen contents also improves the theoretical maximum overall energy efficiency for such a conversion process.

Two different approaches to natural gas conversion can be discerned the so-called indirect and direct routes. A direct route is, for example, the conversion of methane directly into products such as ethane and ethylene by means of oxidative coupling. However, this route gives only relatively poor yields (25–30%) to useful products and development work in this area has largely been abandoned due to poor prospective economics. Furthermore, it is unlikely that a breakthrough will be achieved with new catalyst systems since the desired primary products (ethane and ethene) are less stable than the methane feedstock and are therefore destroyed by gas-phase homogeneous deep oxidation reactions.

In the field of indirect methane conversion a new process (SMDS) to convert natural gas into primarily middle distillate fuels has recently been commercialized by Shell in Malaysia [8]. Natural gas is firstly thermally converted into synthesis gas which is then passed over a specially developed Fischer–Tropsch catalyst which selectively produces high molecular weight hydrocarbon products (Fig. 16). In a second catalytic step these waxy hydrocarbons are selectively hydrocracked to achieve a high yield of middle distillate fuel. This fuel product is of very high quality both in terms of combustion performance and environmentally since it contains no aromatics or heteroatoms. Some high quality hydrocarbon chemicals products such as solvents and waxes are also co-produced in this process.

Future developments in this area will be aimed at reducing the capital costs of such plants and increasing the selectivity towards the desired fuel or chemical products. Catalysis will again likely play a dominant role in developing the next generation of natural gas conversion technology. Reactor technology improvements will also continue in this field and the first generation of fixed bed reactor systems may be replaced with more efficient slurry bed reactors. A research programme to develop such reactor systems is currently being sponsored by DOE in the US also with some industry participation.

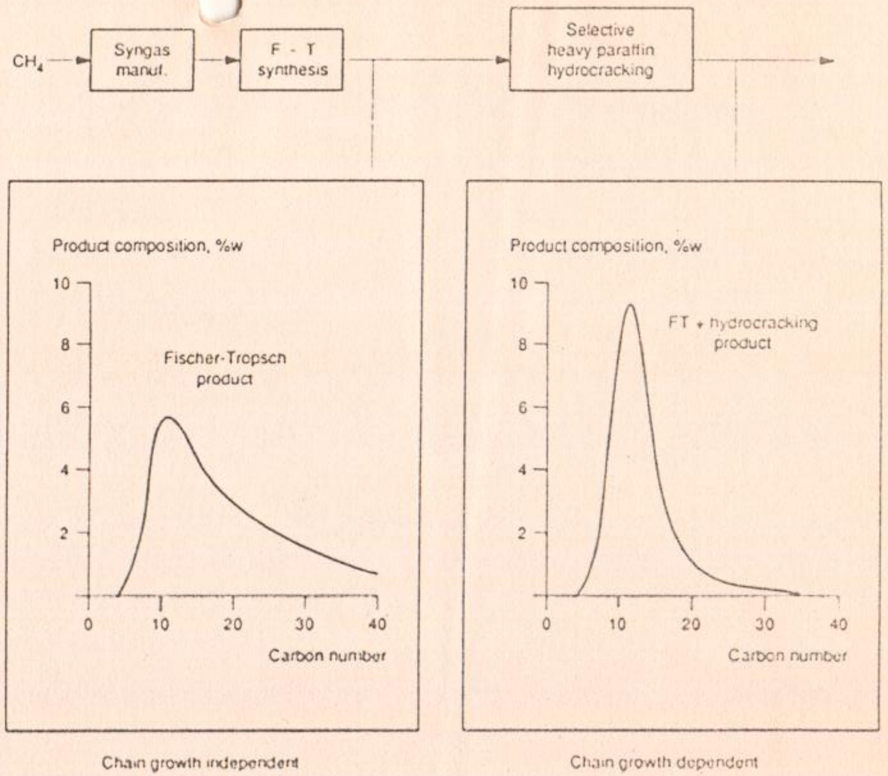


Fig. 16. Process scheme for the Shell Middle Distillate Synthesis (SMDS) process.

The syngas manufacturing step in natural gas conversion processes accounts for a substantial part of the capital and operating costs. Thus, there is considerable incentive to search for more cost effective processes to manufacture syngas. Conventionally, syngas is produced using non-catalytic (thermal) partial oxidation or (catalytic) steam reforming. The choice of process is very often dictated by the desired H_2/CO ratio of the synthesis gas which should preferably closely match the average H/C ratio of the final hydrocarbon product in the syngas conversion step to achieve maximum overall thermal efficiency (Fig. 17).

For example, for the SMDS process where the primary products are relatively high molecular weight alkanes, partial oxidation is the preferred syngas process providing a 2:1 H/C ratio match between feed and product. In such a process pure oxygen rather than air is used to avoid the build-up of nitrogen in the recycle system. The oxygen feed, which is produced by air liquefaction, is a major cost factor and thus the oxygen selectivity of the syngas manufacturing is also an important element of the process.

Hybrid systems involving both thermal (oxidation) and catalytic (reforming) reactor sections are also possible such as the so-called autothermal reforming (ATR) technology which has been commercialized, for example by Haldor-Top-

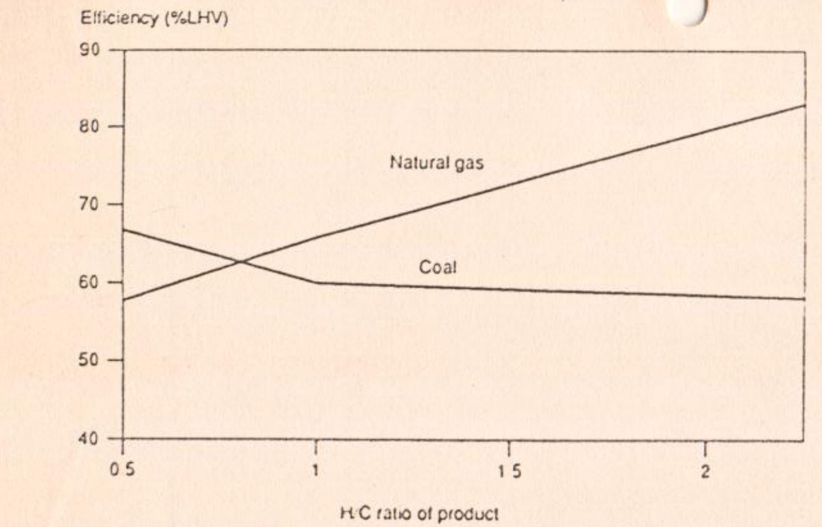


Fig. 17. Thermal efficiency (%LHV) as a function of feedstock and H/C ratio in hydrocarbon product.

soe. The reforming reactor section contains a specially developed nickel catalyst which is resistant to coke deposition and high temperature operation.

Recent work, for example at Minnesota University, indicates that pure catalytic systems may be interesting for partial oxidation [9]. As shown in Fig. 18 results by Professor Schmidt suggest that rhodium on a ceramic foam exhibits a high selectivity to both H_2 and CO at relatively high space velocities and temperatures. The University of Minnesota workers have also proposed a mechanism (Fig. 19) whereby the activation energy for the formation of surface hydroxyl species is proposed to be significantly higher on rhodium compared to platinum

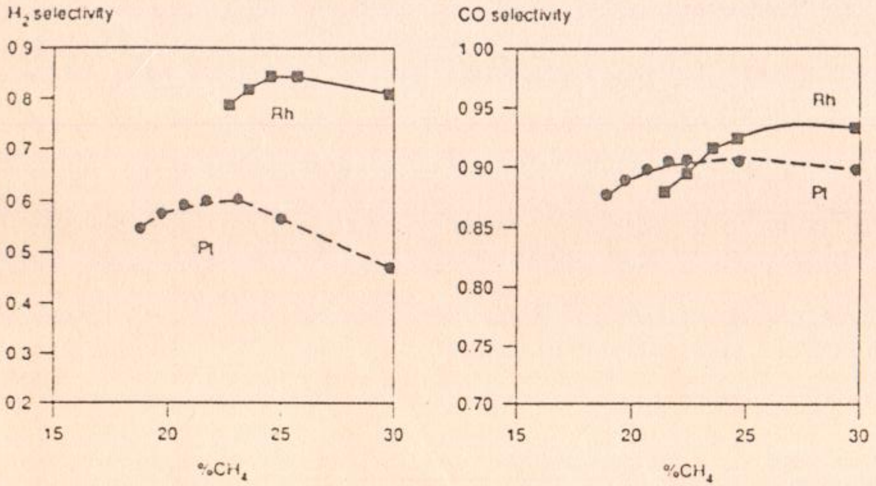
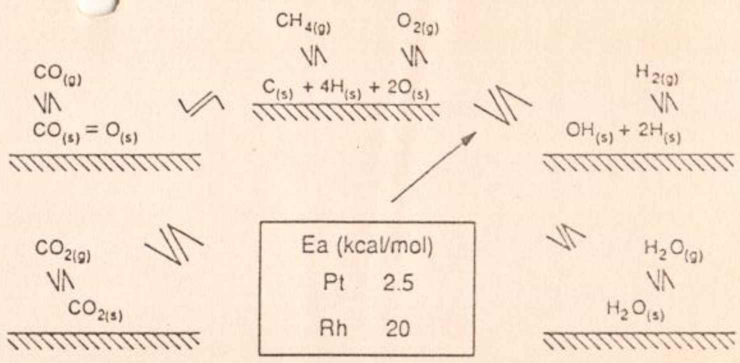


Fig. 18. Catalytic partial oxidation (CPO) of methane to synthesis gas.



Proposed mechanism (Prof.L.D.Schmidt)

Fig. 19. Proposed mechanism for CPO of methane.

which would explain the improved selectivity towards H_2 production over the former catalyst system.

Although considerable further research will be required this field of high temperature catalysis does appear to show some promise for the future.

4. Catalytic emission control

In the field of emission control catalytic technology has played a central role and in recent years there have been some interesting new developments. For example, increasing amounts of H_2S are being produced by refineries which are traditionally removed by the so-called Claus process in which H_2S is oxidized to sulphur over a rather simple alumina catalyst. Recently, based on research carried out at the University of Utrecht in the Netherlands, a new iron based catalyst has been developed (so-called SuperClaus process) which in the last stage of a Claus process effectively removes much of the remaining H_2S thus significantly reducing S emissions to the atmosphere [10].

The catalytic technology for NO_x emission reduction was originally developed in Japan and is termed selective catalytic reduction (SCR). Ammonia is traditionally used as a reducing agent which is added to a NO_x containing emission stream which often contains oxygen from air. The SCR catalyst (e.g. Ti/V or Ti/W on a monolith) reduces NO_x to nitrogen and water. It is, in fact, quite remarkable catalytic chemistry, whereby a reduction reaction is selectively catalyzed in an oxidizing gas phase environment.

The traditional catalysts are based in titanium and vanadium or tungsten usually wash coated onto a monolith support in order to minimize pressure drop across the reactor system. Some more recent developments include a low temperature (about 200°C operating temperature) $DeNO_x$ process developed by Shell research which has the advantage of being an add-on system (Fig. 20). The substantial reduction

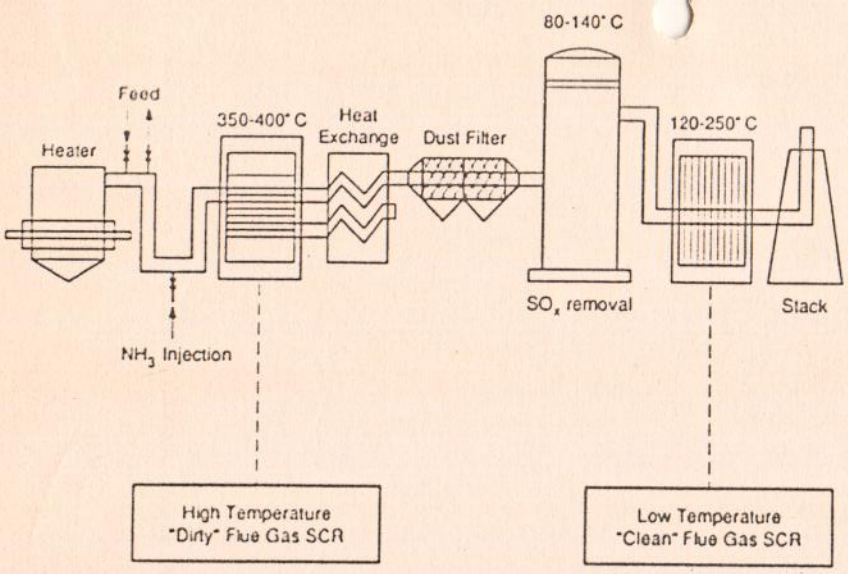


Fig. 20. High and low temperature $DeNO_x$ (SCR) systems.

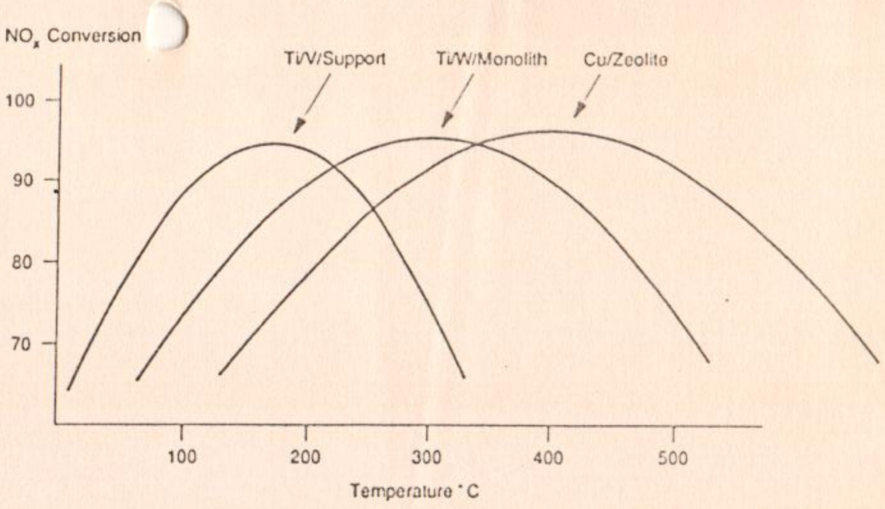
in operating temperature is achieved by means of a highly active Ti/V catalyst system in combination with a novel lateral flow reactor (LFR).

In addition, the operational temperature window for SCR technology has also been extended to the high side. This has been achieved by developing some novel copper–zeolite based catalyst systems (Fig. 21). These zeolitic catalysts [11] have a much lower tendency to oxidise NH_3 to NO_x at higher temperatures. High temperature SCR catalysts are of particular interest for application in natural gas fired power stations where the NO_x needs to be removed from relatively hot effluent gases.

Perhaps one of the most interesting recent developments by Air Products is a cobalt–zeolite based SCR catalyst [12] which, quite remarkably, can operate using a hydrocarbon such as methane as the reducing agent instead of NH_3. These catalysts also perform well when oxygen is present in the NO_x containing effluent.

Also in the field of auto exhaust catalysts there are continuing developments [11]. It is expected that the demands in terms of performance of these catalyst systems (e.g. Pt/Rh on monolith) for the simultaneous reduction of CO, NO_x and hydrocarbons will continue to increase. Lower emissions levels, resistance to poisons such as sulphur and improved stability will provide increasing challenges in this area in the future.

A major challenge in this field has been to develop catalysts which can operate under lean burn conditions. Significant potential energy savings (6–10%) can be realized by the development of lean burn running automobiles. However, this development is impeded by the fact that conventional auto exhaust catalysts only operate effectively under stoichiometric conditions and are therefore unable to



$$NH_3 + NO_x \longrightarrow N_2 + H_2O$$
$$NH_3 + O_2 \longrightarrow NO_x + H_2O$$

Fig. 21. Operational temperature ranges of $DeNO_x$ catalyst systems.

remove NO_x in an excess of oxygen. Recently, some Japanese automobile companies (Mazda and Toyota) have announced that they have developed some new exhaust catalyst systems which operate effectively under lean burn conditions. The Mazda catalyst would appear to be based on a noble metal zeolite system.

Also in the field of catalytic combustion of volatile organics new challenges exist to find systems that will selectively oxidize aromatic compounds and chlorinated hydrocarbons [13]. In addition, a number of companies are actively developing catalyst systems for use in gas turbines. Potentially, catalytic combustion could substantially lower the operating temperature and thereby dramatically reduce, for example, NO_x production leading to primary emission control [14].

5. Future trends

As refineries continue to increasingly convert the heavy part of the barrel the residue fuel product will no longer be exported (i.e. so-called 'no fuel refineries'). Refineries will also need to produce more hydrogen for processing and this will create the need for improved routes for hydrogen manufacturing.

Transportation fuels in the future will be increasingly designed on the basis of molecular composition for both better combustion performance and emission control. 'Super' clean fuels will likely become more widely available, for example, from deep hydrogenation or natural gas conversion processes and the costs of producing these products will likely be reduced in the future by means of improved catalytic technology.

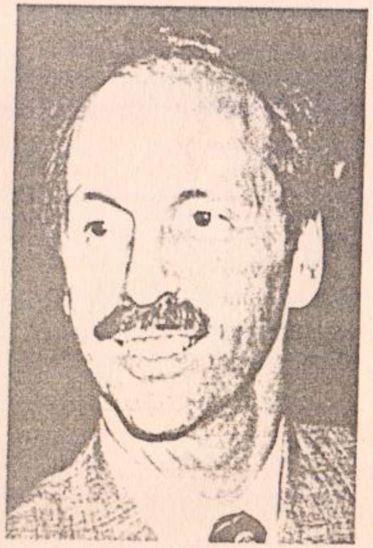
The shift from oil to natural gas as a feedstock for both fuels and chemicals is a trend which will likely be stimulated by both improved technology and reducing oil reserves.

Emission control technologies will continue to develop quite rapidly with a likely shift from secondary to primary control. The development of new high temperature catalyst systems will have a significant impact on, for example, catalytic combustion technology which could potentially be quite widely applied for emission control.

Energy storage and CO_2 emission control will become increasingly important where catalysis will likely be prominent.

In general, catalytic technologies will continue to play a dominant role in the energy related industries particularly as companies strive to meet new environmental legislation in the most cost effective manner.

These developments cannot, however, be achieved by catalysis in isolation. A multiple of disciplines such as catalytic chemistry, computational chemistry, material science, surface science, separation technology, process control, reactor engineering and process technology will all have their role to play.



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