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February 1988
ENGLISH

DEVELOPMENT OF NOVEL SHAPE SELECTIVE ZEOLITE CATALYSTS

DP/IND/87/007/11-02

INDIA

Technical Report*

Prepared for the Government of India
by the United Nations Industrial Development Organization,
acting as executing agency for the United Nations Development Programme

Based on the work of H. J. Lovink
Expert in Preparation of Catalysts

Backstopping officer: M. Derrough, Industrial Operations Technology Division

United Nations Industrial Development Organization
Vienna

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23.02.1988

UNDP Programme NCL-Pune India

by H.J. Lovink

Re: DP/IND/87/007/11-02-J13424

Mentor at National Chemicals Laboratories
Dr. Paul Ratnasamy

Time schedule

As there is a close co-operation between NCL, IPC (Indian Petrochemical Co. Baroda) and IOC (Indian Oil Company) in all research fields that are close to commercial application or - evaluation I also visited the latter two institutes.

Stay in	Period	Activities
	Sunday 24/01	Arrival from Amsterdam.
Delhi	Monday 25/01	Visit to UNDP in Delhi Evening dinner with Dr. Mukhopadhyaya IOC.
	Tuesday 26/01	Afternoon talks with Dr. Ghosh of Indian Oil Company (notified by NCL Dr. P. Ratnasamy) Evening transfer to Pune
	Wednesday 27/01	Received by Dr. P. Ratnasamy, NCL; met all his collaborators and discussed my consultancy job.
Pune	Thursday 28/01	Prepared and held a lecture on 'Novel Zeolites in FCC catalysts'
	Friday 29/01	Prepared and held a lecture on 'Mild hydrocracking of heavy gas oils and the scope for novel zeolites'
	Monday 01/02	Met Director, Mr. Doraiswamy discussed the use of foreign patent information and protection of know-how. Detailed talks with other specialists on preparation of zeolites.

National Chemicals Laboratories, Pune India

Discussion with Dr. P. Ratnasamy and his staff on the "Novel Zeolite Project"

By H.J. Lovink

Period: see time schedule

Summary

I presented two lectures:

a) Zeolites in FCC catalysts.

b) Mild Hydrocracking using novel zeolites as alternative acid catalysts.

Both have been added to this report. A written text was not made in view of the time; the copies of the overhead sheets are giving all the essential information.
Subsequently I had many detailed discussions with Dr. Sivasanker and other staff members of NCL. On some 18 individual technical points I will comment in writing to my hosts in India.

Some remarks

1) NCL has an amazing number of good staff and its instrumentation is very impressive; not many institutes in the world are so well equipped with instruments. It is a pity that power supply to the lab fails so often and I wonder whether more can be done regarding a bigger back-up generator (such as in Baroda!).

2) The work in NCL is not merely scientific but also applied (see the motto in the entrance hall). For this I would advice to acquire a number of (cheap) pulse reactors and test each novel zeolite for a number of catalytic reaction that are still: either using old catalysts or have much room for improvement such as:

- Catalytic reforming
- Catcracking
- C_5 - C_7 hydro isomerization
- Alkylation of C_4's and benzene + propylene
- Oligomerization
- Others like C_4" isomerization etc.

Bombay	Tuesday 02/02	Visit to CATAD zeolite plant in Bombay, see separate report.
Baroda	Wednesday 03/02	Visit to IPCL, Baroda, see separate report
Travel	Thursday 04/02	Travel to from Baroda, to Pune, report writing
Pune	Friday 05/02	At Pune, advised on some papers to be published shortly, with the zeolite group. Advised on silicage/sol as ingredients for zeolite synthesis.
	2 days week-end + 1 day travel Goa, report writing.	
Pune	Tuesday 09/02	Rounding off discussion with Dr. P. Ratnasamy; discussed the role of Feri silicates/Ct. pentsaviles for reforming and proposed simpler methods for preparation
Delhi	Wednesday 10/02	Visit to Indian Oil Company, Faridabad discussion of FCC catalysts using the Novel Zeolite i.e. Dr. Ratnasamy's lab has developed and that "CATAD" can manufacture.
Delhi	Thursday 11/02	Debriefing at UNDP, long discussion with Mr. Islam on my findings. Evening return to Vienna via Bombay, Zürich
Vienna	Friday 12/02	Debriefing in Vienna, Mr. Derrough + administrative staff
	Saturday 13/02	Return (to Holland, later).

H.J. Lovink

P.S.:

CATAD is a zeolites and adsorbents manufacturing facility in Bombay, formerly owned by Associated Cement Co., but recently purchased by IPC-Baroda.

3) More relatively simple catalyst preparation equipment e.g. pelletizers etc. are needed. more attention to the 'chemistry of sols, gels and crystals in statu-nascendi is advisable. This is not costly!

4) Keep an eye on the most recent patent literature, "Derwent Services" for example. This is not costly and advisable since much work of NCL is rather close to commercial industrial practice!

5) Advice on synthesis details, novel structures, raw materials etc.

6) Regeneration of zeolites

During industrial use many zeolites collect a certain amount of coke leading to zeolite deactivation. The Alumino-silicates can be regenerated mostly without much loss in activity.
Other zeolites containing B, Fe, Cr, etc. may not be stable. New techniques could be developed (oxydation-reduction) materials incl. e.g.:

- Incl. of 3-10 ppm Pt for low temperature combustion.
- Hydrogenation-removal of coke.
- Extractions etc.

This will be imperative for real commercial success. (I am ready to consult the group on specific experiments).

NCL - the catalysis and zeolite group has an interesting and promising set of specialization and people, which can generate substantial profits and even royalties for India when an additional organisation is set up for "licensing" and "scale-of technology".
up

H.J. Lovink

Visit to : IPCL - Baroda February 2-3, 1988
Dr. PrasadaRao

By : H.J. Lovink

Summary

We had long discussions on subjects of interest to IPCL.

My impressions:

A complex like Baroda is still busy understanding the backgrounds of the various technologies it has purchased. This is time consuming particularly for R&D. Licensors, many times, cannot (or will not) reveal all these backgrounds required for the economic long term operation of these plants.

The atmosphere and goals of R&D look OK to me. Making a practical choice of the many priorities is needing much attention, as the R&D manpower looks very limited to me.

The purchase of CATAD requires more work for Pradsada Rao and he should form a separate group for this operation with:

1) Some small scale manufacturing equipment such as precipitation, crystallization, extrusion, pelleting etc. equipment.

2) Testing equipment for absorbents alumina's, also pentasil type zeolites.

3) A group leader with dedication, some experience, less "publication oriented" and a feel for engineering.

4) Clever use of advice from overseas manufacturuers can be sought e.g. from high purity alumina producer "Condea" in Germany (which costs nothing, I think).

A more extensive study of the opportunities that existing and new zeolites offer for improvement of the manufacturing processes of IPCL and IOC. Newer technologies should be included such as the coming hydrocracking, improvement in catcracking and catalytic reforming.

The time available to me was too short for going into in any details.

Two requests:

a) Can I send 5 kg of a reforming catalyst carrier to Baroda for experimenting with various noble metals plus the suggested impregnation procedures?

b) Would it be feasible to construct a pilot plant for making 1 ton/day of FCC catalyst?

Both requests will be discussed in Holland by me with the management of Akzo Chemie. The first will be no problem, the second may be taking more time to decide on; (it has no commercial value to Akzo Chemie).

H.J. Lovink

Visit to : CATAD plant for adsorbents and alumina carrier in Bombay February 2, 1988

By : H.J. Lovink

Received by the plant staff of Mr. Lohokare

Summary

CATAD purchase is a good thing for IPCL's further developments, although it will not make money for some years on the present product slate of absorbents.
The employees are skilful though the means are modest and partly outdated, except the flash calciner which is an essential element. It will also be useful for many new products.

The present adsorbents are at least partly not up to world standard because the technology of manufacture is rather primitive (not because of the skills of the staff).

Investments will be necessary, but can only be decided on when a complete plan with alternatives is made. Investment range from US$ 0.5 million to US$ 5.0 approximately, for improving productivity (see later).

Additional instrumentation, technical customer services and sales should be planned for the future.

Close co-operation with Baroda and NCL should be stressed by management, and exchange of personnel is useful.

Modern manufacturing equipment for CATAD will enhance tHe success-chances of zeolites and catalysts of NCL and IPCL. It will also increase greatly the energy efficiency of the operations.

Specific advices

Mr. Lohokare and staff showed me around the adsorbents plant where I remarked:

1) It is not usual in USA/Europe to pre-dry $Al(OH)_3$ prior to the manufacture of Na Aluminate.
   Elsewhere all suppliers can deliver $Al(OH)_3$ absolutely moisture-free. The present operation is very labour intensive and gives loss of raw material!

   Action Lovink: I will send the typical analysis of $Al(OH)_3$ of Alcoa, Kaiser etc. and some recipe to make Na aluminate (published, but good).

2) The dewatering and washing of adsorbents is carried out on a small rotating filter, that works only at low efficiency. For zeolites horizontal filters are much better because the slimy zeolites tend to filter badly and fall off the drum.

   Action Lovink: Will send the names of a few European manufacturers of horizontal filters.

3) A different kind of extruder of the 'Sprout-Waldron type', also called pelletizer based on 'a drum with holes' is probably better as extrudate length now is a problem.
   As alternative a transport belt with a roller could also be tried. This is very empiric though.

4) The calciner looks very energy consuming and may not have a good residence time distribution for extrudates. A rotary indirectly fired Kiln is to be preferred for extrudates.

5) Sizing of balls and extrudates can be improved. This is important for 'world market quality'. Not too costly. This will increase sales in India.

   We have not talked on ZSM, alumina carrier for HDS catalysts and other items.

General remarks

1. Also for absorbents and catalyst manufacture it is very worthwhile to consider import of some machinery such as digestors, filters, calciners, size reduction, sieving, if necessary.

2. The present operation is very low in energy efficiency and high in manpower use: with 134 men we make in Europe 3000 tons HDS catalyst incl. R&D and Technical Services.

Alternatives for streamlining this plant:

a) Better operation as described above, will improve the product quality and capacity. For US dollars approx. 1-2 million this can be carried out in a few steps.

b) Relocation to Baroda: costs of equipments roughly $ 5-10 million.

   Advantage of b): close to IPCL's development center; because daily contact will improve the speed and efficiency of new developments. A much more detailed study seems warranted.

H.J. Lovink

Visit to	:	Indian Oil Corp. Research& Development Faridabad Dr. Sobhan Ghosh, Group Leader (see list of attendees) Dr. Mukhopadhyaya, Director February 10, 1988 (Also discussion with Ghosh on January 26, 1988)
By	:	H.J. Lovink

Summary

The group is focusing on catcracking and has bought an Arco FCC test unit, plus some MAT units. Also self-built steamers and other ancillary testing equipment.
A lab spray drier for catalyst will be followed by precipitation and washing equipment.
I told them how to make FCC catalyst on a small scale and the principle steps for doing it on industrial scale.
They want to make several modificationsof zeolite catalysts in order to make it later "in India". Told them that an economic world scale plant will make some 10.000 tons/year and has $ 75.000.000 investment, according to recent Akzo Chemie experience. Mr. Mukhopadhyaya gave me a good view on India's domestic petroleum- and zeolite production position.

Actions Lovink:

- Provide them with an open literatures FCC catalyst recipe.
- Information on octane analysers.
- Information on the Anderson method.
- Further literature on catcracking and novel zeolites "from the West".

General points

Dr. Mukhopadhyaya, married to a very pleasant Russian wife (at home they speak Russian, Bengali, Hindustani, English and Parsi) hosted me in his home on two evenings, and I have learned a great deal about Indian (oil) industry from him.

Zeolites

The interest can be described in several terms:

a) Conversion of indigenous raw materials to fuels and olefins e.g. ethanol and methanol in times of high oil prices.

b) A certain autarkism, everything small and big that India needs should be made in India; manpower is not a problem.

c) Scientists like this area and like to publish their results as a means to get recognition (in India and the world).

d) Some think zeolites have even more promise than biochemistry (I doubt this).

Indian Oil Co.

A state-owned company that operates a number of refineries needed when oil products consumption started to grow in the years '50-'80.
The former Shell (now Bharat) and Esso (Hindustan) refineries were nationalized but not amalgamated into IOC, and they have a more or less independent life.
IPC, Indian Petrochemical Company, in Baroda is closely connected with Indian Oil Co., because of the petroleum feedstocks used from the adjacent Gujarat refinery.

The oil scene is very different from that of the usual "stagnant" - "half depressed" atmosphere in the US, Europe and Japan.
The economy is growing as is visible for everyone coming back after 5 years: oil consumption rises rapidly some 5%/year due to industrial but particularly scooter use. Refiners are planning expansions and modifications like in Europe in the years '60/'70!

Petrochemicals and gasoline are showing very similar trends. The former also grow outside India, sothat certain shortages can be expected if action is not taken quickly. Here in India state companies in which ministries have an important say are in a complexer situation than say Bayer, Exxon, Shell, Hoechst etc. in that the decisions and financing take much more time.
Much of India's petrochemicals has to be imported (approx. 40%)

Nevertheless the atmosphere in this young research center is one of "humming activity" of enthusiastic young people directed by experienced Dr. Mukhopadhyaya. Since 15 years the place in Faridabad is in operation with lube oil blending research, 10 years they have a very impressive field test unit for rheology of Bombay high crude (only Shell has a larger one!) and some 2-3 years ago they started in newly erected extensions with Fluid Catcracking and zeolite catalyst manufacture.

There were <u>numerous detailed questions</u> regarding FCC manufacture. One of the requests was for a good laboratory - and pilot plant catalyst manufacturing procedure that has been published in the literature and can be considered reliable.
I will send one of the US patents and underline the good procedure (Action Lovink).

<u>Assisting</u> at the discussion in the laboratories of Indian Oil Co., Faridabad, Thursday February 11, 1988;

Dr.	S.G.	(Sobhan Ghosh)	-	1	
	V.K.	(V. Krishnan)	-	2	
	S.K.R.	(S.K. Roy)	-	3	synthesis of zeolites + cat
	A.K.D.	(A.K. Das)	-	9	
	Y.V.K.	(Y.V. Kumar)	-	8	refinery contact man
	V.B.S.	(V.B. Shende)	-	4	
	R.M.T.	(R.M. Thakur)	-	5	
	G.S.M.	(G.S. Mishra)	-	6	
	I.K.D.	(I.K. Dixit)	-	7	

+ Private discussion with Director Dr. Mukhopadhyaya.

General remarks UNDP assistance
Novel zeolites - Pune

Spare parts

Many scientific instruments are in operation in NCL and the technical staff is doing a fine job with them. However, unavoidably spare parts are needed, because of the normal wear and tear or unintentional mishandling. Especially in high pressure equipment valves will start leaking after a while and replacement will be required.
The present administrative procedure for NCL is very complicated and direct help of UNIDO by means of a special budget and telex or telefax ordering with a copy of the brochures' essential pages will make it much more efficient.
In this respect NCL is much less well situated than comparable laboratories in the developed countries. With efficient management of such a system total costs to UNIDO need not be higher, rather lower as less spare parts will be required at the original purchase.

Packing

Suppliers of instruments should be notified of the additional handling hazards of trucking of sensitive instruments in India. Dismoutning to smaller individual pieces is desirable. Damage to instruments means delay of many months in India!

Novel zeolites

Although we all hope that absolutely unique novel zeolites will be developed in India, we should realize that many new zeolites will be "brothers and sisters" of types invented in the rest of the world, sometimes almost simultaneously.
For pure scientific purposes this is not a point of concern, but as soon as application work to practical industrial processes or model reactions shows remarkable new reaction pathways, the matter is important and due consideration should be given to;

- Patents in the industrial world (USA, Europe, Japan).
- Possible infringement of other patents.
- Combination of the new know-how with related existing technology.
- Licensing and process development, not only in India.

NCL can expect considerable competition from the rest of the world:

Particular attention should be given to the so-called multinational companies that can react extremely rapidly when a novelty is emerging anywhere (Mobil, Union Carbide, Shell, Dupont etc.).
I see no safeguards in the project description in Mr. Henry J. March's project document of April 30, 1987, in this respect!

Certain complex reactions will be better understood, more zeolites or "crystalline structures with regularly interspaced accessible surface" will find more application also in sequential reactions.

<u>Opportunities</u>

There still are a number of old catalytic systems for which no new "novel zeolite catalyst" have been found yet, such as:

- Alkylation of iso-butane with butylenes to so-called "alkylate".
- Alkylation of benzene with propylene.
- Low temperature isomerization of so-called light naphtha.
- Oligomerization at catcracking conditions and 1-3 seconds contact time.
- Hydrodenitrogenation of heavy oils.
- Combination reactions, e.g. the combination of oligomerization and dehydrocyclisation of paraffins.

H.J. Lovink

28/1/88
Pune

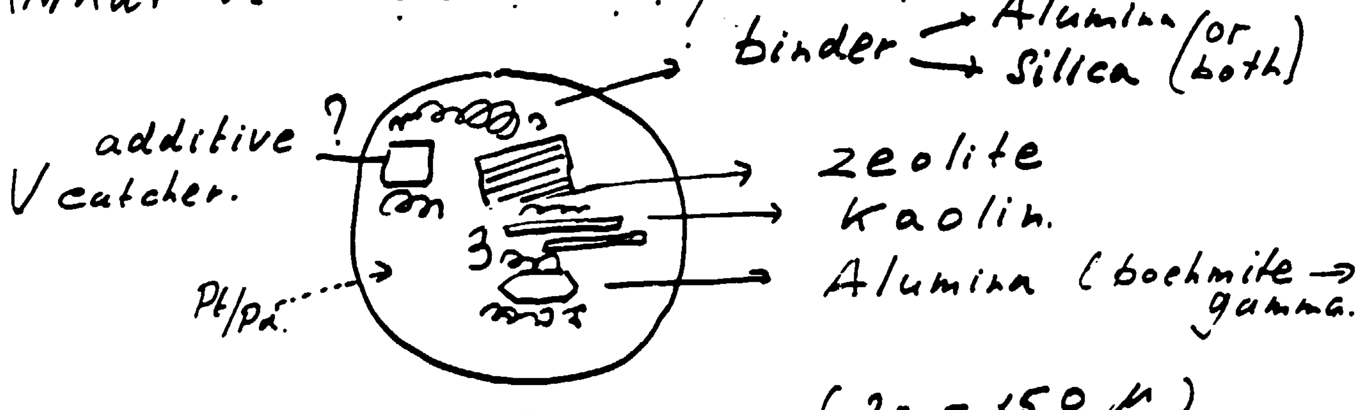
Zeolites in FCC catalysts

H. J. Lovink

UNDP → Ketjen Catalysts

- FCC
- Hydroproc.
  - HDS
  - Hydr Cr.
  - Ref. etc.
- PetroCh. Cats.

) What is FCC catalyst:



<– 65μ –> (20 - 150 μ)

Important characteristics ;

— activity -selectivity
— stability
— hardness, low losses.

3) Requirements for FCC catalyst manufacture: on these components:

- Small particle size 1-5 microns
- no mutual disturbances
  - via waterphase (washing)
  - hydrothermal 700-800°C
- good 'response' to binder or to binder additives.
- stability before spray drying

c) Manufacturing Scheme(s)

Each manufacturer has his own scheme; but roughly two different schemes exist:

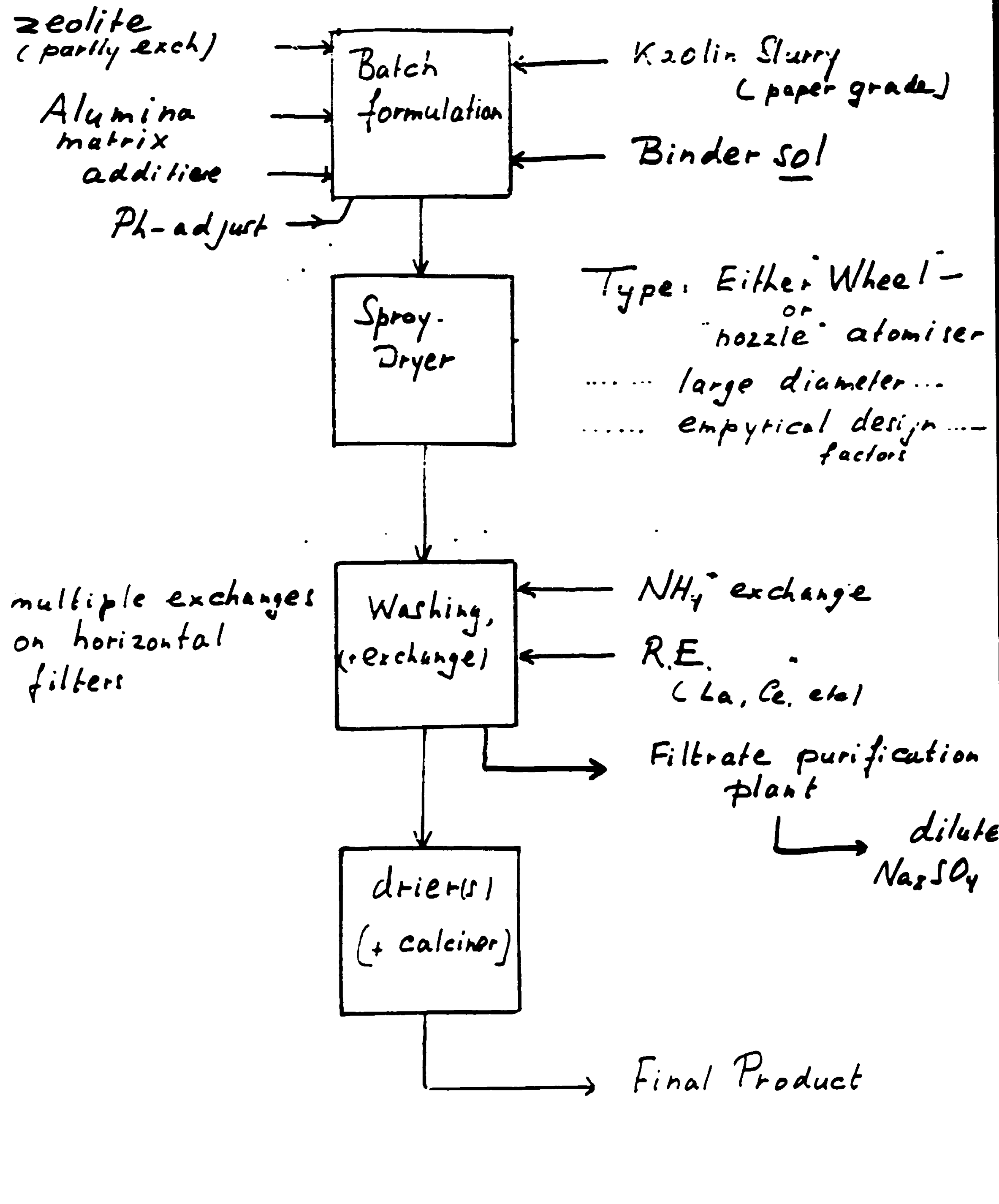
- Grace / Katalystiks / Crosf. / Ketjen (+Filtrol)
- Engelhard

1) The Engelhard scheme only in US, starts from Kaolin → spray dry → calcine → crystallise insitu → wash, exchange → dry
No details in literature.

So far: only one (big) plant (2 installation

2) Grace / Katalystiks (U.C) / Crosf / Ketjen etc

General picture (see Grace Patents expired)



D) <u>Size of operations</u>

Typical FCC cat. plant 25000 - 40000 ton

US plant :	13
Europe . :	4
Japan/Austr :	2
~	19 plants

World market :

	U.S.A. 10^3 ton/y	= 120
	Europe	= 60
	Brazil	= 20
	Rest World	= 50
Total	thousand mt/y	: 250

Plant occupance typical <u>75 - 90%</u>

→ Capacity depends on grade

→ Grades become more "time consuming"

Average plant inv. 25000 t/y now
~ $ 75.000.000

5 years ago:

~ $ 40.000.000 or less
irrespective of US $ devaluation!

E. Zeolite types

1) Faujasites

They constitute the real cracking part of FCC (except for maybe "heavy resids")

— Types all derived from NaY of
- SiO_2/Al_2O_3 ratio 4.8 - 5.5 (approx)
- Crystal size 1-5 microns

Preparation techniques vary. (are secret)
based on waterglass
sodium aluminate

temperatures: 100°C
crystal. times: 5-15 hrs

[Good literature: see textbooks and patents (mostly expired)]

Intermediate agents:
- Silica sol / gel
- Cryst. seeds
- ph. adjustment.

After crystallisation:
- de water
- wash.
- re work filtrate

Zeolite types (Cont'd)

— In use in FCC catalysts:

- CREY

NaY ~2x exch. with $RECl_3$, calcined (Na_2O at 4-5%)

- USY

NaY repeatedly exch NH_4^+, calc, exch NH_4^+ and finally steam calcined. ultra stabilisation. (Maher patent)

— "Modified (cleaned)" USY

The newest zeolites, only partly commercialised since 1-2 years.

methods* → Al extraction
→ higher NaY - Si/Al
→ Silica enrichment

Many actual catalysts are containing Mixtures of above technologies eg

- CRE-USY

or

- CRH(RE)Y etc.

depending on market demand

* [Scherzers' review.]

Organisation Zeolite Development in FCC plant(s). [Molsieve group]

Three groups :

1) R&D fundamental studies
Small lab scale equipment **synthesis**

Purpose :- chemistry of crystallisations
- mechanisms, types,
- treatments, exchanges etc

2) Pilot plant group.
1-10-100 l batch equipment,
filters, dryers etc

Purpose :- process studies, recycles, drying, calc. conditions
- preparation of 1-10 kg samples
- scale-**up** recipes of lab
- scale-**down** problems of plant

3) Plant tech service group
- not responsible for daily operations
- Follows daily operations of FCC plant, solves technical problems.
- Evaluates procedures.

2) Additive Pentasil (ZSM-5)

Only small application compared to Y sieve

- ZSM is mixed with matrix, sol and spray dried

- Purpose: aftercrack gasoline paraffins

  linear C-C-C-C-C-C-C etc

  or

  C-C-C-C-C etc (branched, with C on the second C)

  to C_3'' and C_4''

Process in FCC Unit not very selective (500°C)

RON increase 1-3 no's

C_5^+ yield decrease 2-3% gasoline.

Zeolite characterisation

Plant control:

- Analytical, SiO_2/Al_2O_3, Na_2O, RE_2O_3
- Physical
  - crystallinity
  - "ph" in water
  - SA, part size
  - Ao

Infrequently:
- performance in catalyst
- NMR, EXAF etc.

FCC catalyst types

Three general groups:

1) Vac. Gasoil → High conversion
   - max gasoline + LCO (- LPG)
   - min coke
   - throughput max

Catalyst: - CREHY, little matrix high activity*

* KMB. low act. for max LCO = low conversion

2) Vac gasoil → Higher conversion
   - max Octanes, iC_4"
   - low coke

Catalyst: USY or CRE USY + some alumina Matrix

3) Vac Gasoil + resid (Ni+V ≈ 3 ppm
   - min coke
   - max throughput
   - max Cat. stability, metals resistance

Catalyst: (RE) USY + some matrix + metal catcher.

Note: Individual Catalyst types have a life of only 3-4 years; some 50% much shorter. Some 10% 5 years+

Major elements of FCC catalyst manufacture

Raw Materials
- alum; Na aluminate
- $RECl_3$ sol.
- Kaolin slurry
- H_2SO_4 dil. $(NH_4)_2SO_4$

Zeolites
- Crystallisation
- washing
- liquids reworking
- drying; calcining

Alumina's
- preparation
- washing, conditioning

Batch formulation
- automation on components
- batchsequence, temp, Ph's, time

Spray drying
- particle size
- roundness

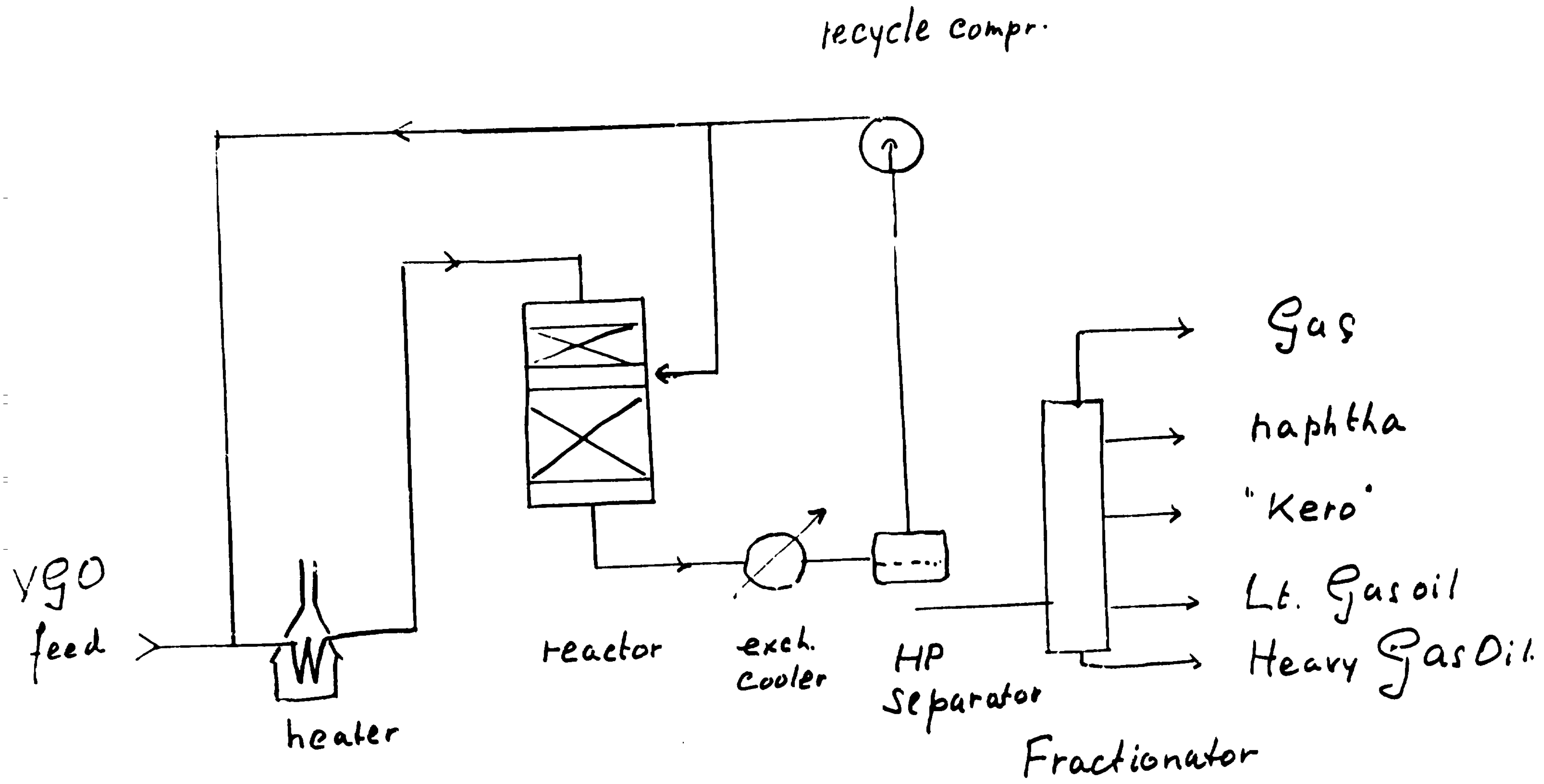
Washing
- exchanges

Drying Calc

Environmental
- filtrates
  - recycle NH_3
  - $RE(OH)_3$
- solids, dust collection reworking.

Quality control

Cost control, Maintenance, Manpower etc


recycle compr.
Gas
naphtha
"Kero"
Lt. Gasoil
Heavy GasOil
VGO
feed
heater
reactor
exch.
cooler
HP
Separator
Fractionator

Mild Hydrocracking of Vacuum Gasoils. (MHC)

- "Mild" = lower pressure (40–70 bar)
- " = lower conversion, temp's.

		HDS	MHC	Hydr. Cr.
Pressure	bar	60	80	150
Reactor temp	°C	330-370	380-420	400+
H_2 : oil	Nm^3/m^3	300	300	1000+
LHSV	hr^{-1}	0,5–15	0.3 - 1	0.5
% HDS		90	98-85	98+
% HDN		70	85-70	95+
% Conversion		5	20-40	90+

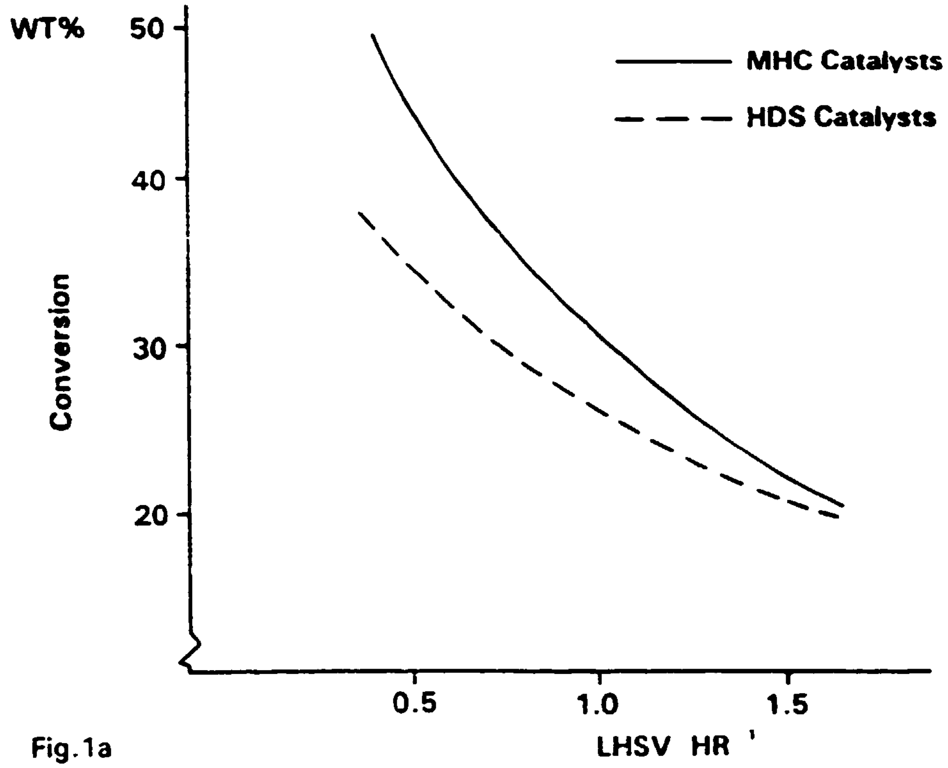

WT%
50
40
30
20
Conversion
MHC Catalysts
HDS Catalysts
0.5
1.0
1.5
LHSV HR⁻¹

Fig.1a

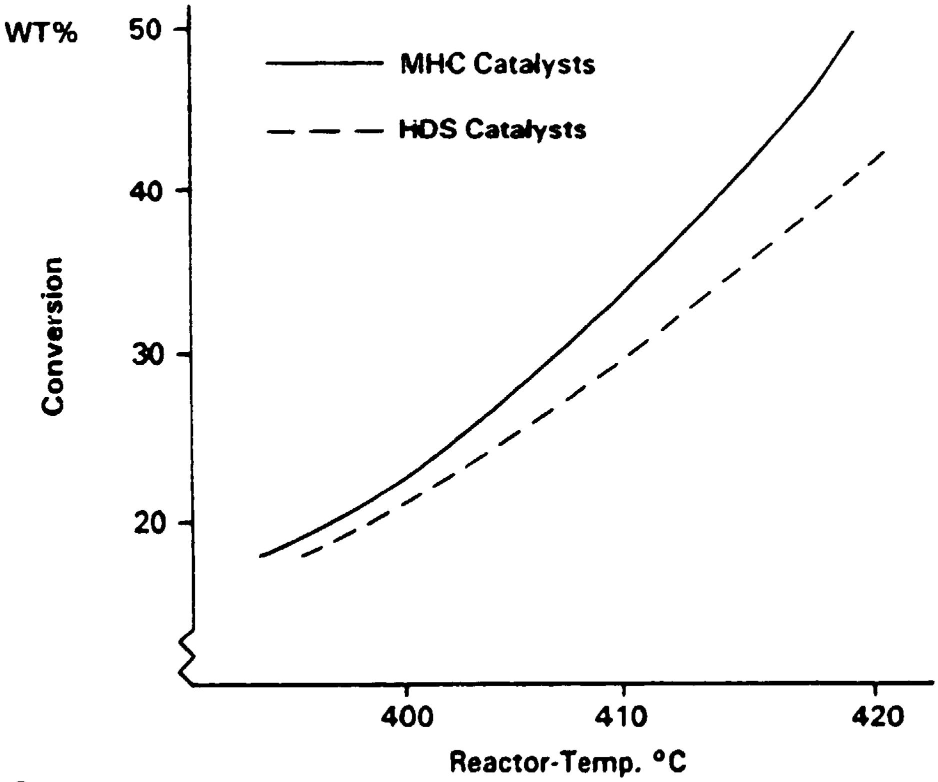

WT%
50
40
30
20
Conversion
MHC Catalysts
HDS Catalysts
400
410
420
Reactor-Temp. °C

Fig.1b

Table 2. Typical analyses of catalysts

			HDS catalyst Grade KF 742	MHC catalyst KF 1011
Chemical composition				
LOI	(550°C)	wt%	2.0	1.0
MoO_3		"	15.0	12.0
CoO		"	4.2	-
NiO		"	-	5.0
Na_2O		"	0.10	0.05
SO_4		"	1.5	1.0
Fe		"	0.03	0.03
Carrier		"	<--- activated alumina --->	
Physical properties				
Surface area		m^2/g	260	270
Pore volume		ml/g	0.51	0.40
Estimated Reactor Density		g/ml	0.60	0.75
Side crushing strength		lbs/mm	4.0	3.0
Diameter		mm	1.15/1.35	1.6
Average Length		mm	3.2	4.0
Abrasion		%	1.0	1.0

Hydrotreating – MHC catalyst preparation

Carrier Preparation →
Precipitation of hydroxydes (al – silica)
↓
Dewatering, washing.
↓
Spray drying

Formation Particles →
Mix-mulling of carrier powder, ext. aid (HNO3), water, dust
↓
Extrusion to 1.5 - 3 mm particles

Calcining →
Drying, sieving
↓
Calcining, sieving

Impregnation →
P.V. saturation with solutions of NH_4 molybdat[e]
Co Nitrate or
Ni Nitrate – Moly – $PO_4^{\equiv}$ soluti[on]

Drying Calcining →
Drying
Calcining

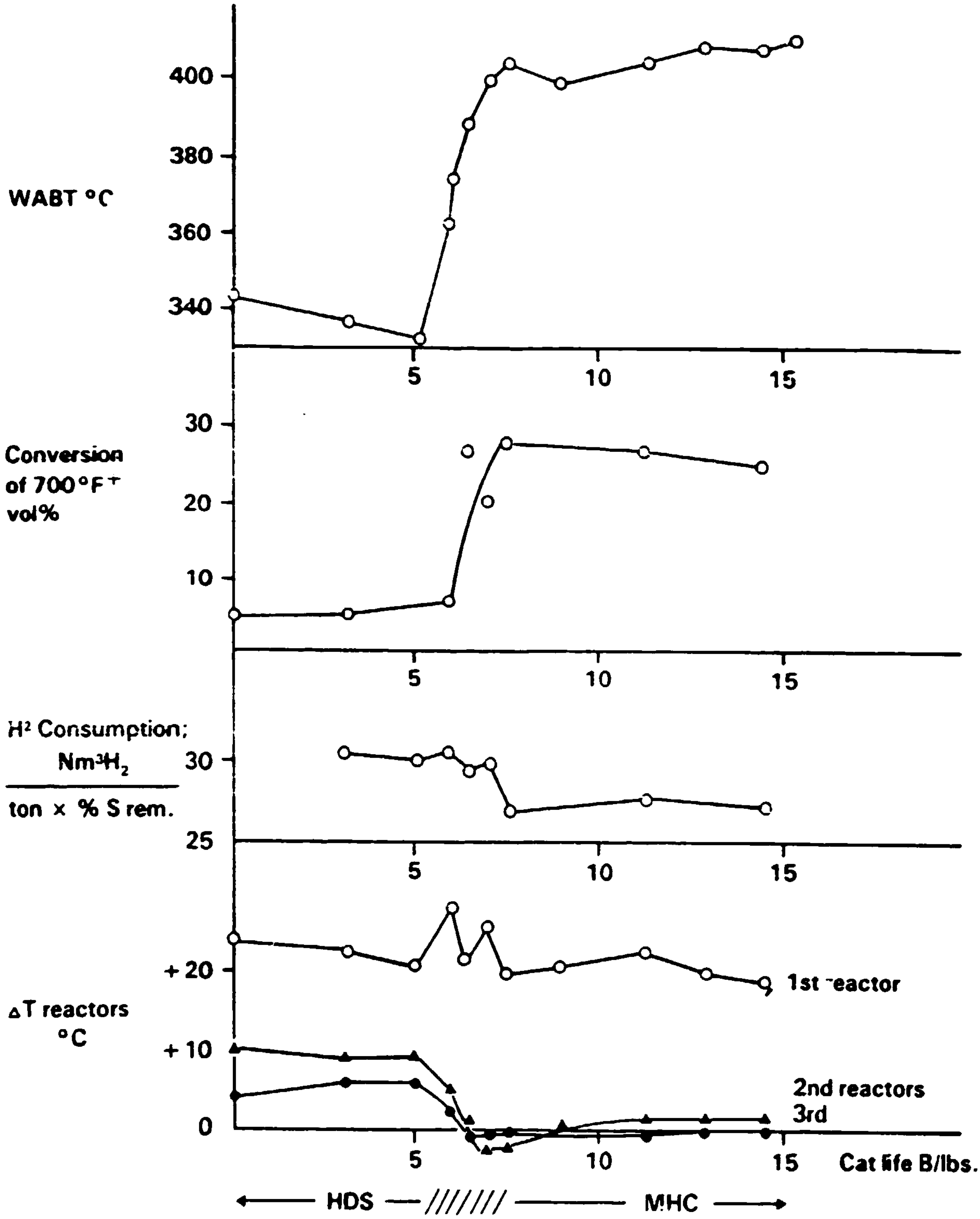
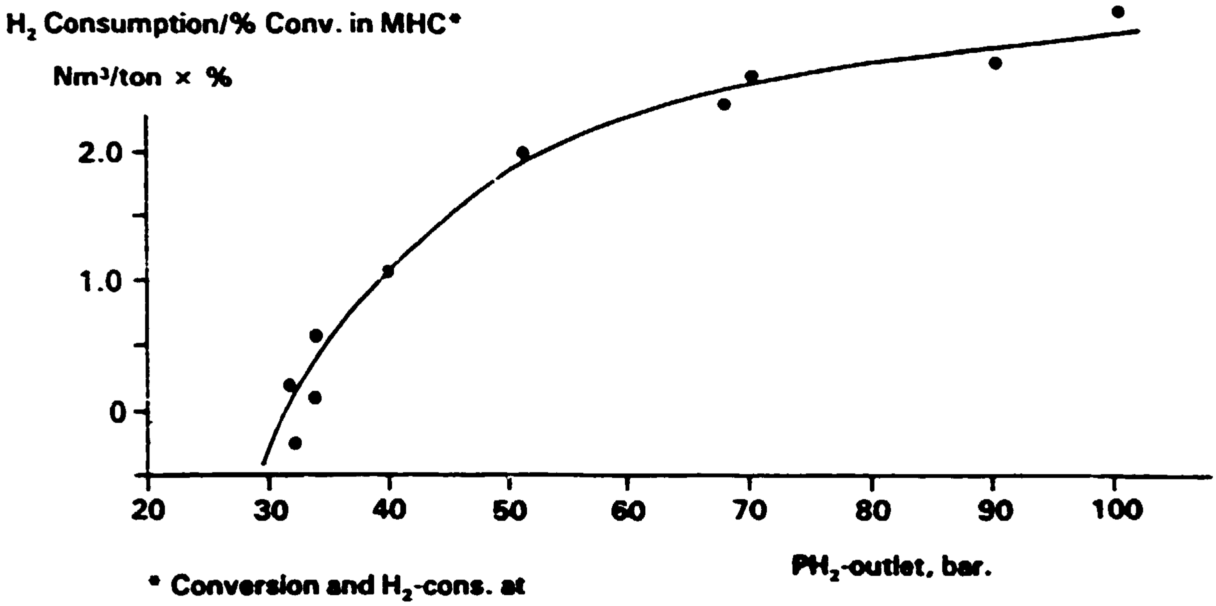


Fig.6 b

Switch from HDS to MHC;
VGO; KF 165

Y =



* Conversion and H$_2$-cons. at HDS conditions subtracted!

Fig 1

<— HDS conditions - - - - - - - - - - - Full Hydrocracking conditions ·····>

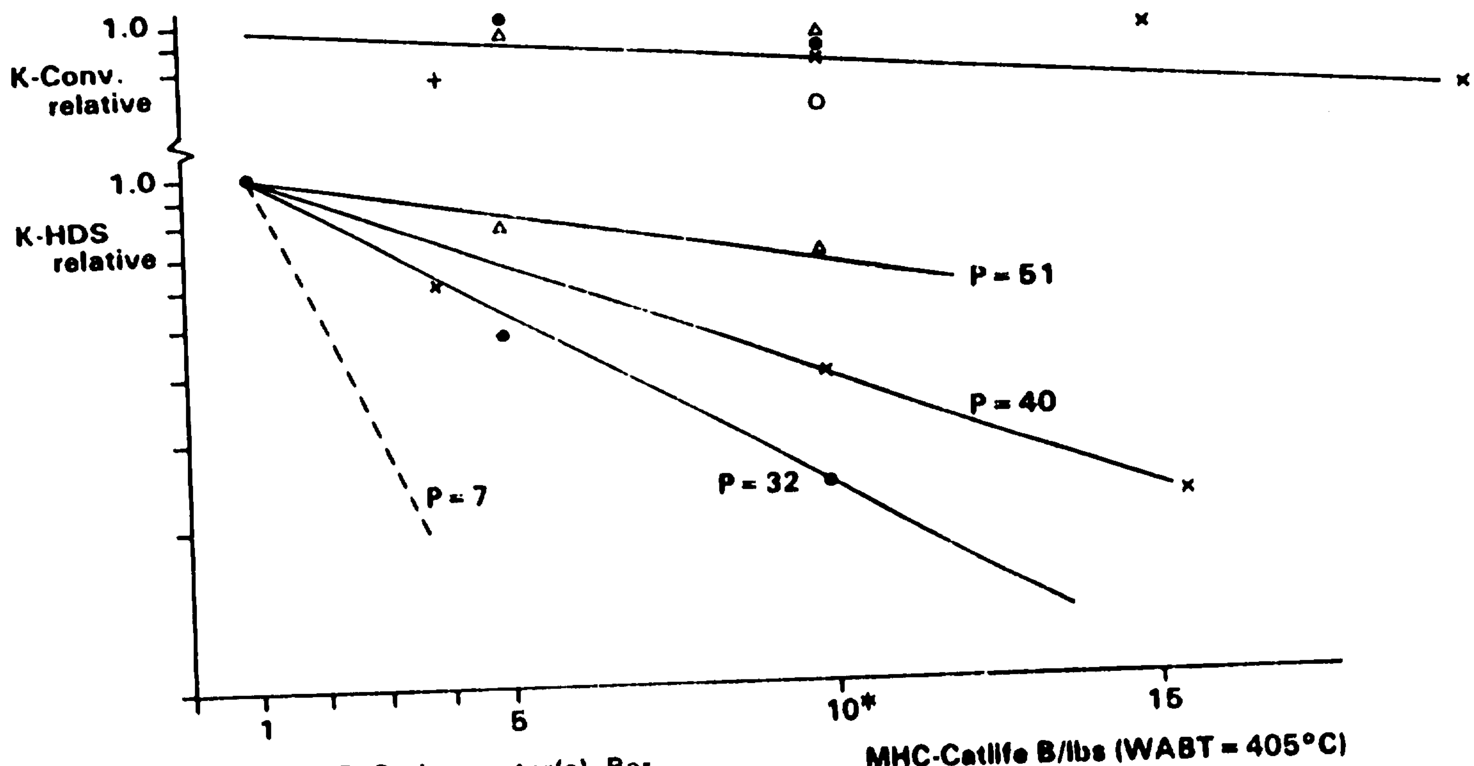
$$Y = \frac{(H_2\ \mathrm{cons})_{MHC} - (H_2\ \mathrm{cons})_{HDS}}{(\mathrm{Conv\%})_{MHC} - (\mathrm{Conv\%})_{HDS}}$$

At low pressures:

naphthenes ⟶ aromatics + H_2 !

H_2 + S comp → H_2S

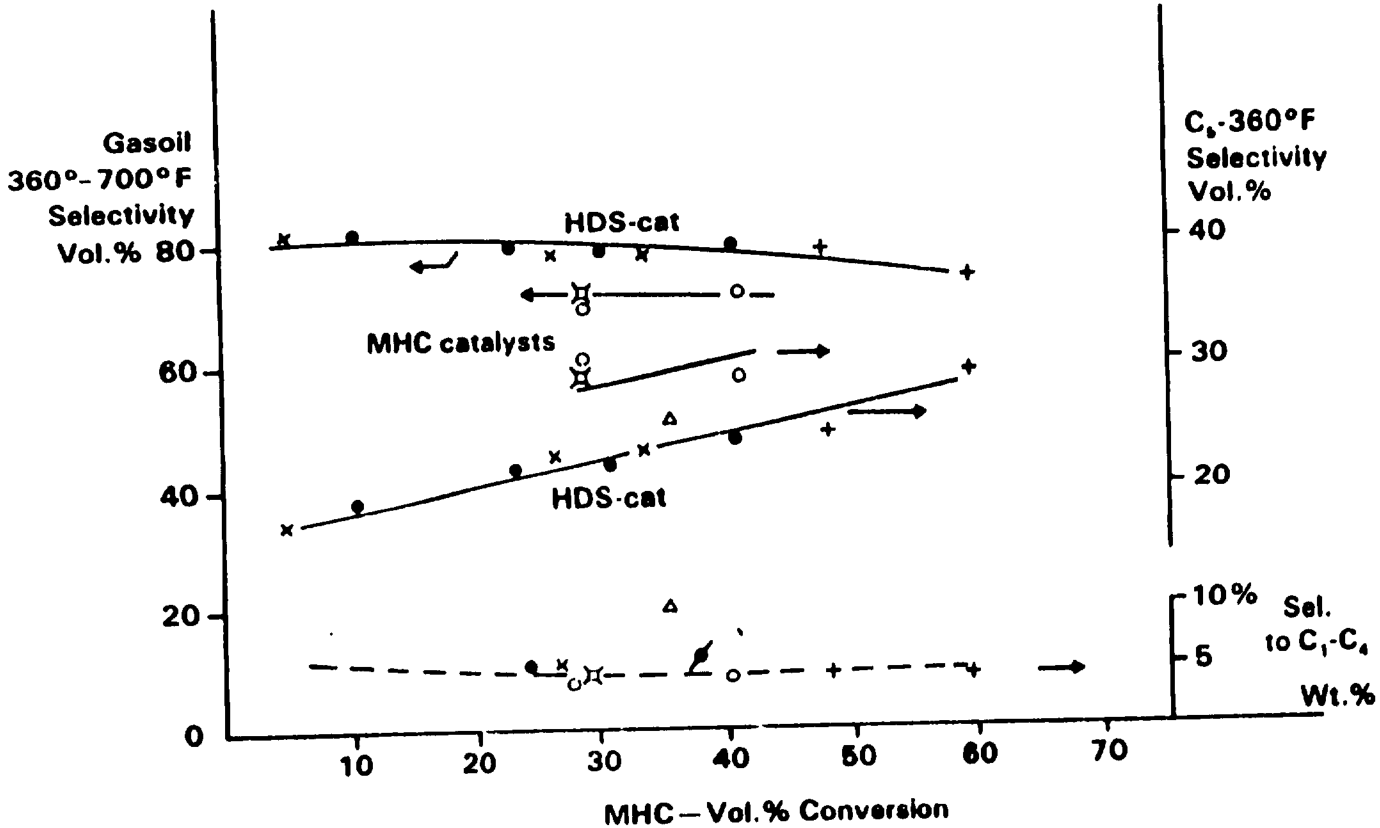
but ... little extra coke deactivation !



$P = H_2$ P.P. Outlet reactor(s), Bar

* = 315 Ton/kg.

Fig.5



Gasoil
360°-700°F
Selectivity
Vol.%
80
60
40
20
0
HDS-cat
MHC catalysts
HDS-cat
C_5-360°F
Selectivity
Vol.%
40
30
20
10%
5
Sel.
to C_1-C_4
Wt.%
10
20
30
40
50
60
70
MHC – Vol.% Conversion

Fig.6a

Table 4. Properties 1*, 2* of light gasoil, kero and naphtha

	Light gasoil			kero		naphthas			
H_2 part pressure bar	density g/ml	cetane[3*] index	S/N ppm's	smoke mm	density g/ml	br. no	aromatics vol %	S/N ppm's	density g/ml
30	0.88	37-42	200/100	12	0.85	2-3	30	300/50	0.78
50	0.88	40-45	100/50	14	0.83	0.5	25	150/5	0.75
70	0.89	45-55	30/10	17	0.84	-	-	50/2	0.75
100	0.80	55-65	-	25-30	0.78	-	3-5	5/	0.71

1* Feed is ME-VGO's: 2.5% S, spec. gravity 0.920 g/ml

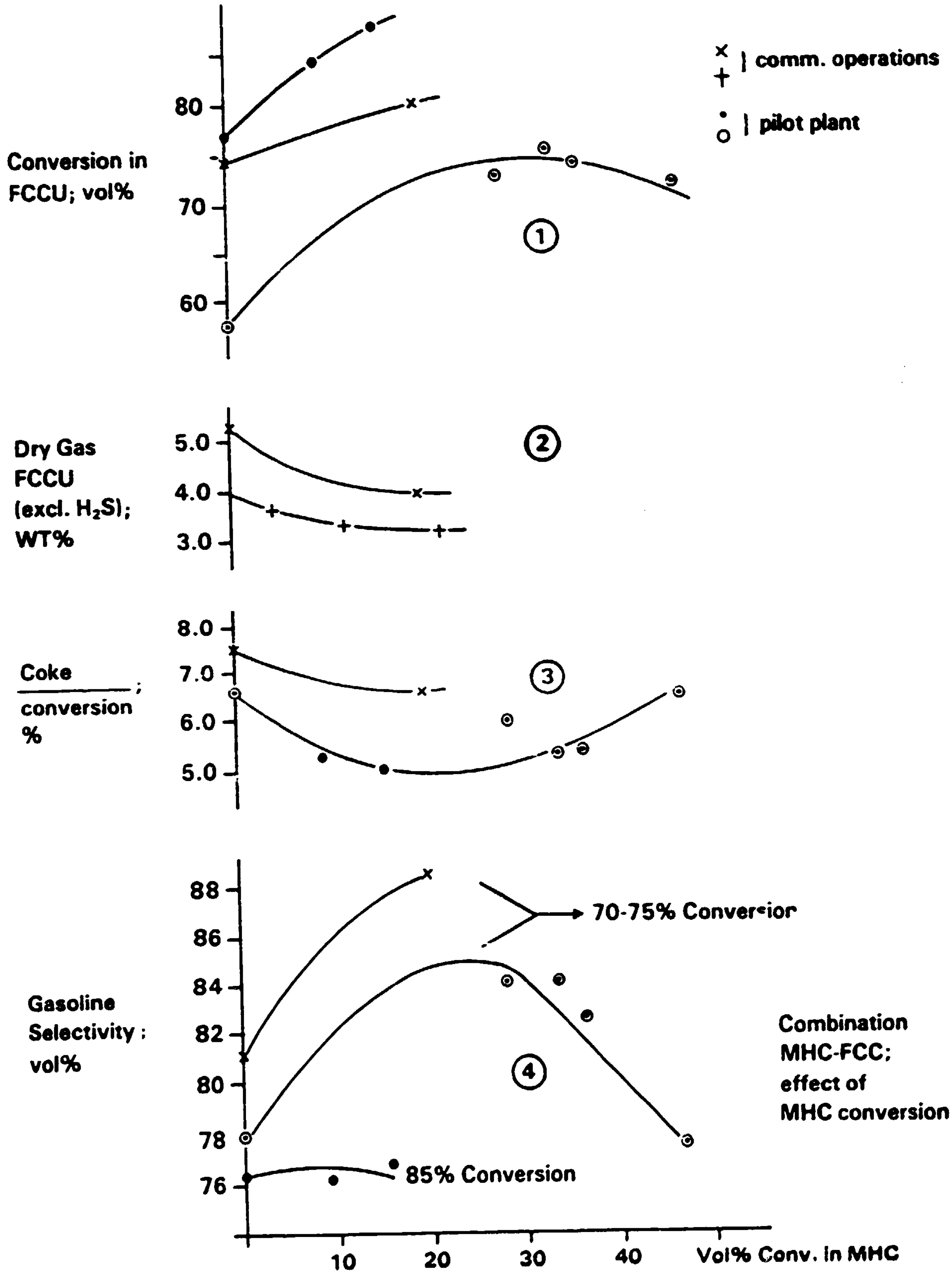
2* Properties at 20 - 50% conversion: 410°C max.

3* Can vary more widely, dependent of LGO still in the feed

Table 5. Properties of ("unconverted") 700°F$^+$ gasoil

H_2 part pressure bar	S/N[1] ppm's	Concarbon reduction eg. from % → to %	Viscosity reduction c. st.	Density reduction g/ml from ---> to	UOP K Factor change from – to
30	500/500	0.25 --> 0.10	10 - 20%	0.920 --> 0.900	11.90 - 12.10
50	300/200	0.50 --> 0.07	30 - 40%	0.920 --> 0.883	11.80 - 12.10
70	70/15	0.80 --> 0.00	40 - 50%	0.920 --> 0.890	11.80 - 12.40
100	20/5	-	-	0.920 --> 0.870	11.80 - 12.60

1 Feed is ME-VGO's: 2.5 S, spec. gravity 0.920 g/ml



× + | comm. operations
• o | pilot plant
Conversion in FCCU; vol%
80
70
60
①
Dry Gas FCCU (excl. H_2S); WT%
5.0
4.0
3.0
②
Coke / conversion; %
8.0
7.0
6.0
5.0
③
Gasoline Selectivity; vol%
88
86
84
82
80
78
76
④
70-75% Conversion
85% Conversion
Combination MHC-FCC; effect of MHC conversion
10
20
30
40
Vol% Conv. in MHC

Fig.8a

CATALYTICA

HIGHLIGHTS

Volume 13

Number 4

WINTER 1987

A Look at Catalytica's 1987 ACT Seminar

Madan Bhasin of Union Carbide questions Farrel Lytle about applications of EXAFS.

Nobel Prize winner Jean-Marie Lehn talks about his ground-breaking work in supramolecular catalysis.

New Large-Pore Molecular Sieves Have 18-Member Rings

A new large-pore molecular sieve termed VPI-5 was claimed by M. Davis and J. Garces of Virginia Polytechnic Institute at a conference in Belgium in September, and earned coverage in the technology column of a subsequent *Wall Street Journal*. Davis' research in this area is supported by Dow Chemical Co. and because patents are still pending, full details about the synthesis, structure, composition, and characterization of VPI-5 are not available. It is claimed to have pores created by 18-member rings, the same 81(1) net structure proposed by Smith in 1984 and discussed in Catalytica's 1984 zeolite study. VPI-5 has a pore diameter estimated at 13–14 Å, significantly larger than those of other molecular sieves or zeolites used to catalyze cracking of crude oil fractions to more valuable products such as motor fuels. The larger pore size of VPI-5 suggests that it might allow large petroleum components access to internal catalytic sites that are inaccessible in existing materials. This might lead to increased conversion to high value-added products. Unfortunately, it appears that VPI-5 is primarily composed of aluminum phosphate, and lacks acidic sites able to catalyze cracking reactions. It should also be noted that such larger feed components have lower H/C ratios and a greater tendency to form coke, which would produce a low catalytic lifetime for VPI-5 should it be active. Nevertheless it will be interesting to learn how such large pores are generated; the use of a hydrophobic template cation is a popular speculation. Some eminent zeolite experts call this report a major breakthrough, but applications are still to be identified and exploited.

87-079313/11 E19 H04 J04 (E33 J01) MOBI 19.12.83
MOBIL OIL CORP *US 4647-442-A
21.08.84-US-642966 (+US-562778) (03.03.87) C01b-15/16
C01b-33/28

Synthesis of crystalline silico-phospho-aluminate MCM2 - using a two-phase reaction medium

C87-115193

H(4-F2) J(1-D4, 4-E4) N(5-A) E0002
E(31-P2C)

Reclassified and Issued in Section E in Week 87/39.

A synthetic crystalline silicophosphoaluminate molecular sieve material, designated MCM-2, is prepd. by:

(a) providing a mixture comprising a liquid organic phase (I) consisting of an organic solvent immiscible with water and a silicon source soluble in the solvent, and a liquid aq. phase (II) comprising dissolved or partially dissolved $AlPO_4$-5 crystalline aluminium phosphate; the mixture further comprising a tetraethylammonium directing agent;

(b) maintaining the mixture under conditions for crystals of MCM-2 to form; and

(c) recovering the MCM-2.

USE

MCM-2 has substantial ion exchange and catalytic properties. It may be used, opt. after ion exchange, as catalyst for organic conversion reactions e.g. conversion of paraffins to aromatics, alcohols to hydrocarbons, alkylation of aromatics, catalytic reforming, hydroisomerisation of n-paraffins, olefin or aromatic isomerisation, reduction of oil pour point, hydrogenation-dehydrogenation, desulphurization and olefin polymerisation.

WIDER DISCLOSURE

MCM-2 is novel; it is of general formula:

$$M^{m+}_{x/m} : (AlO_2)^{-}_{1-y} : (PO_2)^{+}_{1-x} : (SiO_2)_{x+y} : N^{n-}_{y/n}$$

M = cation of valence m; N = anion of valence n; x and y are greater than -1 and less than +1; if x = 0, then y is not 0; if y = 0, then x is not 0; if atomic ratio Al/P is greater than 1, then (x+y) is greater than 0.001 and (y + 0.6x) is less than 0.4; if atomic ratio Al/P is less than 1, then (x+y) is greater than 0.001 and (x+0.5y) is less than 0.5.

Occluded organic material may be present; cations present are readily exchanged with other cations. Directing agent used in prepn. may be tetrapropylammonium hydroxide or bromide or other onium cpd.

US4647442-A+

PREFERRED METHOD

The organic solvent is a 5-10C alcohol. Directing agent is tetraethylammonium hydroxide. $AlPO_4$-5 is described in US4310440. Reaction takes place at 100-200°C in 24-168 hrs.

EXAMPLE

A two-phase mixture was prepd. consisting of: organic phase 60g. 1-hexanol and 10g. $Si(OC_2H_5)_4$; aq. phase 23.1g. H_3PO_4 (85%), 10g. Al_2O_3 and 71g. water. 37g. Tetraethyl ammonium hydroxide and 2 ml. 0.05 M CsOH were added as directing agents; pH was 6.5. The mixture was heated for 144 hrs. at 180°C. Crystals of MCM-2 were obtained (X-ray diffraction pattern given).(9pp16*4RKMDwgNo0/0).

[illegible]

Major players in this area

- Mobil
- Union Carbide
- Exxon, Shell, Dow, UOP and others

[illegible signature]

US4647442-A