

VAPOUR EXTRACTION OF HEAVY OIL AND BITUMEN

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Introduction

The world's total estimated proved reserve of conventional oil is one trillion bbl and the world average of the reserves-to-production ratio is only 46 years at 1990 production levels^[1]. This excludes the reserves of heavy oil, tar sands and bitumen that amounts to 6 trillion barrels of oil in place which are not economically recoverable with present technologies. If the proper technology is developed for extracting these resources it can supply the fuel demand for the next few centuries.

Heavy oil and bitumen have high viscosity and low API gravity. In some reservoirs, such as Athabasca, the oil viscosity is in millions of mPa.s at reservoir conditions making conventional recovery impossible. Flooding techniques cannot enhance recovery substantially, due to the adverse mobility ratio.

The viscosities of the heavy oil and bitumen decrease drastically with increase in temperature. Among the thermal recovery processes applied to produce these crudes, the Steam Assisted Gravity Drainage^[2] proved to be very successful. In this process steam is injected through a horizontal well and the hot oil being less viscous drains by gravity to the horizontal production well. Using long horizontal wells, very high production rates can be achieved in this process.

In steam processes the energy efficiency is poor due largely to heat losses to the underburden and overburden (specially in thin reservoirs). Enormous amount of effluent is to treated, a huge source for the supply of fresh water is required, clay swelling due to contact with fresh water from the condensed steam causes formation damage. However, instead of steam, if solvent is used to dilute bitumen some of these problems can be eliminated.

Butler and Mokrys^[3] studied the extraction of bitumen with toluene in a line source Hele-Shaw cell. On the basis of the magnitude of different physical properties affecting the production rates, it was concluded that the solvent leaching would be slower than the thermal processes. It was anticipated that vaporized solvent in combination with deasphalting may enhance the rate considerably.

Concept of the Vapex Process

In the Vapex (vapour extraction) process vaporized hydrocarbon solvents are injected in the reservoir through a horizontal injection well. The solvent initially dissolves in bitumen around the injection well until diluted oil breaks through the horizontal production well placed vertically below the injection well. Solvent vapour rises slowly to form a vapour chamber in the extracted sand matrix above the injection well. Solvent vapour dissolves in bitumen at the solvent bitumen interface, diffuses through the bulk of bitumen and the diluted oil drains to the production well by gravity. The use of vaporized solvent produces higher driving force in gravity drainage and also reduces the residual amount of solvent in the extracted reservoir. The concept of the process is shown schematically in Figure 1. Several other configurations of injector and producer wells are also possible.

Selection of Solvent and Conditions

In this process production rate is directly related to the amount of solvent dissolved and diffused into bitumen. One important aspect of this process is deasphalting that yields in situ upgraded oil reducing many down stream problems. The extent of deasphalting also depends on the amount of solvent. The solubility of a vaporized solvent is maximum near its dew point pressure. Hence, the solvent pressure should be as close as possible to its vapour pressure at the reservoir temperature. If the dew point pressure of the solvent is lower than the reservoir pressure solvent liquefies and fill the extracted sand matrix with liquid solvent. Thus a barrel of oil is replaced by a barrel of liquid solvent which is not economic. Hence, to be suitable for the process, the solvent should have a dew point pressure slightly higher than the reservoir pressure so that it can be safely injected without liquefaction and the maximum solubility can be achieved at the same time. This criteria

combined with the abundant reservoir pressures and the cost and availability of the solvents limits the choice of solvent to ethane, propane and butane. In our experiments it was observed that performance of the process with ethane is inferior to that for propane and butane. Propane and butane yields comparable rates. However, propane upgrades the oil by deasphalting which is less prominent with butane. There are many heavy oil and bitumen reservoirs where the pressure is in the range of propane dew point pressure. In shallow reservoirs butane may be suitable.

Theory

The pseudo-steady state model developed by Butler and Mokrys^[3] modified for the process using vaporized solvents predicts the production rates as

$$q = 2La\sqrt{H} \quad (1)$$

where

$$a = \sqrt{2kg\phi^{1-m}\Delta S_o N_s}$$

and

$$N_s = \int_{c_m}^{c_i} \frac{\Delta\rho D_s (1-c_s)}{\mu c_s} dc_s$$

- H = height of the reservoir
- L = length of horizontal well
- q = production rate
- k = Permeability
- g = acceleration due to gravity
- ϕ = porosity
- ΔS_o = change in oil saturation
- μ = viscosity of mixture at solvent concentration, c_s
- $\Delta\rho$ = density difference between solvent and bitumen
- D_s = intrinsic diffusivity of propane in bitumen
- c_s, c_i, c_m = mole fraction of solvent at different points in the boundary layer (Fig. 1)
- m = cementation factor

Since the production rates are directly proportional to the vapex parameter, 'a', it can be used to evaluate the performance of the process at different conditions^[4]. Both the production rates and 'a' are proportional to the square root of permeability and this relation can be used to scale up the production for different permeabilities.

Experiments in Hele-Shaw cell and Packed Visual Model

Several experiments were carried out in Hele-Shaw cell by Das and Butler to assess the impact of asphaltene deposition on the performance of the process. The experimental set up, procedures and the method of analysing data were described elsewhere^[4]. The photograph of the Hele-Shaw cell at the end of one interesting experiment carried out with Lloydminster heavy oil and propane is shown in Figure 2. The propane pressure in this experiment was varied by approximately 10 psi by varying the temperature of the propane supply cylinder between 19 and 22°C as shown in Figure 3. It was observed that at higher pressure, close to the dew point of the solvent, asphaltenes were deposited and at a lower pressure diluted oil drained without asphaltene precipitation. The alternate dark bands (deposited asphaltenes) and white bands (clean swept area) in Figure 2 clearly show the history of the pressure cycles. The corresponding vapex parameters, plotted in Figure 3, shows that the production rate is enhanced when asphaltene precipitation takes place. This due to the tremendous reduction of viscosity caused by deasphalting. Results of some experiments carried out in Hele-Shaw cell with different permeabilities are presented in Table 1. These show that under identical temperature of cell and propane, vapex parameters are proportional to the square roots of permeability.

Several experiments were carried out in visual packed cell using sands of different permeabilities and butane as a solvent. Experimental set up and procedure are described elsewhere^[5]. Cumulative productions from one of this experiment carried out with Peace River bitumen is shown in Figure 4, which is similar to the production profile in all of these packed cell experiments. As expected it is observed that the solvent vapour initially rises to form the solvent chamber, chamber grows to the top of the packed cell and then spreads sideways.

Comparison of Hele-Shaw and Packed Cell Results

Table 2 shows some results of the experiments in Hele-Shaw and Packed cell with Peace River bitumen. The production rates predicted for the packed cell on the basis of the results of the Hele-Shaw cell experiments and the experimental rates are presented in column 4 and 5 respectively. It shows that in the porous media the process goes approximately 10 times faster than expected.

Mechanism of the Vapex Process in Porous Media

The basic mechanism of the process involves the following steps:

1. Dissolution of solvent vapour at the solvent-bitumen interface
2. Diffusion of the dissolved solvent into the bulk of bitumen
3. Dissolved and diffused solvent dilutes the viscous oil and reduce the viscosity
4. If the solvent concentration is high enough the oil is deasphalted in situ
5. The diluted (and deasphalted) oil drains to the production well by gravity

Although the basic process mechanism is same in Hele-Shaw cell and in porous media in the later, the process takes place in a contact zone, instead of at a smooth interface as is the case in the former. This provides a very high interfacial contact area that yields a high mass transfer rate of solvent into bitumen^[5]. The mass transfer is enhanced by capillary imbibition and the corresponding surface renewal. Although the diluted bitumen has a lower surface tension, due to its low viscosity it is quickly drawn away from the interface exposing a renewed interface of fresh bitumen to the solvent. If we consider diffusion of a solvent in a semi-infinite slab of bitumen, the transient concentration profiles and the corresponding mass flux at the solvent-bitumen interface with time are shown in Figure 5 and 6 respectively. It should be noted that as the concentration profile builds up, the mass transfer rate drops drastically. In the Butler Mokrys model it is assumed that a pseudo steady concentration profile is developed in the diffusion boundary layer and each point on the interface moves at a constant rate. This pseudo-steady profile represents a lower mass transfer rate which is probably true in case of Hele-Shaw cell. However, in porous media, with the periodic surface renewal, the early transient mass transfer is more prominent. Even with the periodic renewal, the interface will move at a constant rate resembling the pseudo-steady state. Hence the overall pseudo-steady state analysis will still be valid, although a very high diffusion coefficient is to be used to match the actual mass transfer rate.

Viability of the Process

The production rate scaled up for a pair of 1000 m long horizontal injector and producer in a 5-darcy Lloydminster reservoir (10 m thick) is 850 BOPD and Peace River bitumen reservoir (40 m thick) is 450 BOPD using propane as a solvent. These production rates seem to be economic for field operation. For reservoirs of different thickness and permeability, the rate would vary in proportion to the square root of the vertical thickness and permeability. Although the solvent requirement is 0.5 g/g of oil produced, most of this is recycled back and only a tenth of the solvent-vapour is left behind to fill the reservoir. The energy requirement for this process is only ~3% of that in the steam process. Hence, the process can be successfully implemented for field operations.

Conclusion

1. The Vapex process can avoid many inherent problems of thermal processes.
2. Better quality oil is produced due to in situ upgrading caused by deasphalting.
3. Production rates could be economic.

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Vapour Extraction of Heavy oil and Bitumen

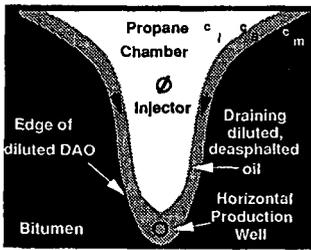


Figure 1. Concept of the Vapex Process

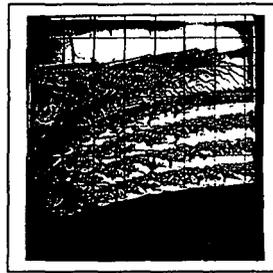


Figure 2. Pressure variation in Hele-Shaw cell (Lloydminster oil and propane).

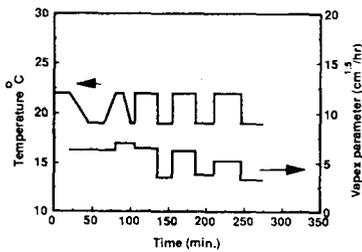


Figure 3. Pressure cycles and corresponding Vapex parameters.

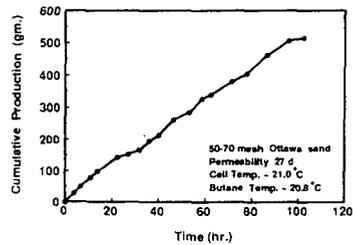


Figure 4. Extraction of Peace River bitumen in 27 d sand.

Table 1. Effect of Permeability on the Vapex Parameter

Crude & solvent	Cell and propane Temperatures (°C)	Cell permeability (d)	Vapex parameter (cm ^{1.5} /hr)
PR and propane	25.0 / 21.7	1344	1.28
		5376	2.47
PR and propane	25.0 / 20.8	3441	1.27
		5376	1.76
LM and propane	25.0 / 20.8	1344	1.66
		5376	3.56

Table 2. Comparison of Results of experiments with Peace River bitumen and butane in Packed Cell and Hele-Shaw Cell.

Cell/ solvent Temp. °C	Cell & permeability (d)	Vapex Parameter (cm ^{1.5} /hr) Exptl.	Flow rates Predicted (gm /hr)	Stabilized rates Exptl. (gm /hr)
25.0 / 25.0	Hele-Shaw (5400)	0.68	-	-
21.0 / 20.6	Visual (830)	1.39	2.22	20.6
22.8 / 22.1	Visual (217)	0.64	1.13	9.5
21.5 / 20.8	Visual (43.5)	0.29	0.47	4.3
21.0 / 20.8	Visual (27)	0.17	0.41	2.5

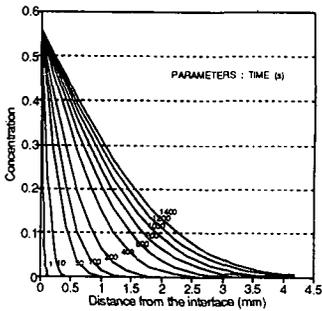


Figure 5. Transient Concentration Profiles

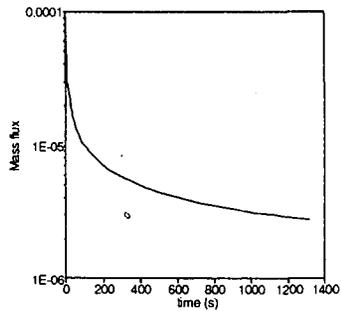


Figure 6. Transient mass flux at the interface

EFFECT OF POLYOLEFINS ON THERMAL CRACKING OF HEAVY RESIDUES

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INTRODUCTION

Polyolefins, like polyethylene (PE), polypropylene (PP) and polystyrene (PS) represent a major source of plastic waste. Annually in Canada, approximately 50 kilograms of organic waste per person is post consumer plastic and over 40% of this plastic is PE. Less than 5% of the latter is recovered or recycled. However, the PE as well as the PP are the richest polyolefins in hydrogen content; they have the highest H/C ratio, both in term of atomic (1.96) and weight ratio (0.17) of all polymers. This represents a tremendous waste of resources. In an effort to use these resources many different processes are at various stages of development and new innovations continue to be introduced in plastic waste conversion (1-5). Most of them are pyrolytic processes which involve the conversion of polymeric wastes to monomers, chemicals, liquid and gaseous fuels and coke by heating the polymeric material to high temperature without oxygen or in a limited oxygen atmosphere. The decomposition temperatures for PE, PP and PS range from 400°C to 450°C (6). Thermal decomposition of PE and PP is a radical mechanism. Random rupture of C-C bonds in the backbone of the chain yields free radicals (7). PS decomposes thermally by a mechanism which involves a hydrogen transfer at the site of scission. The bond scission is random and yields one saturated and one unsaturated molecule (8).

The objective of this present work was to determine the effect of these radicals produced from polyolefins on the aromatic radicals produced from the heavy residues (vacuum bottoms and bitumen) by analyzing the final effects on thermal cracking products, distillates and coke. A series of experiments has been undertaken using a tubing bomb reactor of 100 mL capacity. The experiments were conducted at 460°C or 470°C for 10 min under an inert atmosphere (N₂).

EXPERIMENTAL

Feedstocks

Cold Lake vacuum bottoms (CLVB) and Athabasca bitumen were used as heavy residues. The polyolefins used as additives were PE, PP and PS, pure resins. The elemental and proximate analyses are given in Table 1. Distillation of the heavy oils to determine pitch content (+525°C) was carried out using an automated D-1160 unit.

Batch reactor unit

The reaction vessel was a 100mL stainless steel tubing bomb reactor. The reactor was charged with 20 g or 30 g of heavy residue mixed with polyolefins at various concentrations. The air from the reactor was purged using high pressure nitrogen. Subsequently, the reactor was depressurized to 1atm at room temperature and then the reactor was immersed in a fluidized sand bed preheated to 500°C. At 460°C or 470°C the reaction was continued for 10 min. The reaction time was defined as the residence time at the desired temperature neglecting the preheating periods that increased with polyolefins concentrations from 6 to 10 min. During reaction, the system is agitated by a pneumatic vibrator which assured good mixing. After 10 min the reaction was stopped by rapidly cooling the reactor by spraying with cold water mists. The gases were vented to a gas sampling bag. The remaining slurry was weighed and distilled or extracted with solvent, toluene or tetrahydrofuran (THF).

Product analysis

Process gases were analyzed by gas chromatography (GC) for H₂, H₂S, CO_x (x=1 or 2) and hydrocarbons up to C₅. The slurry products were distilled using an ASTM D-1160 apparatus to obtain the overall distillable and residue products at a cut point of 525°C (977°F). The overall distillable has been fractionated to determine the amount of naphtha (IBP-185°C), light gas oil (LGO, 185-335°C) and heavy gas oil (HGO: 335-525°C). The residue (+525°C) fraction from D-1160 distillation was extracted by THF for determination of coke which is reported as tetrahydrofuran insolubles (THFI).

The liquid products were analyzed by GC using a capillary gas chromatograph (Perkin-Elmer, Sigma 2000), with a flame ionization detector (FID) and capillary column. Toluene solubles (TS), toluene insolubles (TI), tetrahydrofuran solubles (THFS) and tetrahydrofuran insolubles (THFI) were separated by soxhlet extraction.

RESULTS AND DISCUSSION

The significant feature of this study is the conversion of waste plastics (PE, PP and PS) into transportation fuels, i.e., gasoline or diesel fuel in the presence of heavy residues, through a thermal cracking route. The objectives were to increase the distillate yield, to reduce the amount of residue and to reduce the formation of coke during the thermal cracking process at high temperatures and short residence times. The selected operating conditions must favor the cracking of both feedstocks and additives (polyolefins). Without an external hydrogen source and any hydrogenation catalyst, coke formation would be inevitable at high temperature (460°C or 470°C) even if the reaction time is short (10 min). Any increase in distillate yield or suppression of coke formation can be explained in terms of radical interactions during thermal cracking. The interactions of long aliphatic radicals with aromatic radicals from heavy oils compete with coke formation and other retrogressive reactions. The hydrogen donor ability of polyolefins would convert heavy oil to distillate. The qualities of the distillates produced varied depending on the combination of polyolefins/heavy oils, but this aspect is not addressed in this paper.

Heavy oil feedstocks and polyolefins

Two different feedstocks were used for this study. One is CLVB, which contains a high amount of pitch, 83.2%, high microcarbon residue and high content of sulphur. The H/C atomic ratio is 1.42 and the metals content is low. The second one, Athabasca bitumen, has 52.4% pitch and a lower microcarbon residue. Its H/C atomic ratio is 1.57. The polyolefins were pure, with no additives. The PE (HDPE) has a H/C atomic ratio of 1.96 that is very close to that of its monomer (2.00 for C_2H_4). The PP has H/C ratio of 2.00 and PS a H/C ratio of 1.01.

Effect of polyolefin concentration on product distribution

Distribution of the products obtained by the thermal cracking of Athabasca bitumen in the presence of different polyolefins (PE, PP and PS) at 460°C and 10 min residence time under nitrogen atmosphere is shown in Table 2. A comparison of polyolefins performance based on product yields was made by using polyolefins concentrations, from 0 to 20 wt %. The first four lines of Table 2 show the composition of the reactants in terms of bitumen and polyolefins concentrations. The distillate yields including losses show an increase from 67.3 to 75.5 wt %. Losses are considered as light distillate. The non-distillable material decreased from 27.1 to 18.2 wt % for the run containing 13.5 wt % PE and 6.5 wt % PS. Asphaltenes + preasphaltenes (THFS from distillation residue) yields were almost constant for 20 wt % polyolefins additions. The mixture of PE and PP had a slightly lower effect on residue quality compared with 20% PE. Coke (THFI) yield was constant for the three polyolefins concentrations and 32% lower than the run without polyolefins (Figure 1). The amount of gases increased in the presence of PE+PP and PE+PS compared to PE only. The distribution of products obtained from CLVB in the presence of PE is shown in Table 3. For these runs the distillates were not analyzed, the study concentrated on preasphaltenes (THFS) variation and coke (THFI) suppression (Figure 2). A significant effect on THFS was observed at 5% PE compared to 0% PE. The coke yield decreased with increasing PE concentration. Yields of gases in the presence of PE were almost constant with one discrepancy at 15% PE.

The final pressure at reaction temperature decreased with increasing polyolefins concentration. Table 4 shows final pressures for selected runs in the presence of PE. The gas composition indicates an increase in hydrogen consumption.

Effect of polyolefins concentration on distillates

The composition of distillate products (IBP-525°C) for selected runs are shown in Figure 3. The addition of polyolefins resulted in a significant increase in the naphtha fraction including the loss. However, comparable HGO fractions were obtained for the five runs. Naphtha fraction was the highest (45.3% of the total distillate) in the presence of PS. Minimum increase of 1.7% of distillates was estimated for a 20% addition polyolefins (Table 2).

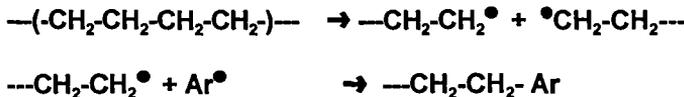
Effect of polyolefins concentration on coke suppression

Figure 4 shows the effect of polyolefins on coke suppression for selected runs using Athabasca bitumen at 460°C. The mixture of bitumen with PE+PP appears to be the

best polyolefins combination for coke suppression with a maximum coke suppression measured at 20 wt % of polyolefins. Using CLVB and PE only the coke suppression effect was more pronounced (Figure 5). At 20% PE the coke suppression was 44.7%. However, an increase of only 10°C in reaction temperature can offset the effect of polyolefins on coke suppression (Figure 6).

Interpretation of effect of polyolefins on products

At the reaction temperature (460°C) the polyolefins are cracked to produce long chain aliphatic radicals. These radicals can interact with aromatic radicals from heavy oils. The aliphatic radicals play the role of scavengers for aromatic fragments and prevent the recombination of large aromatic radicals to form coke, as follows:



Formation of Ar-Ar (coke) was limited by the interaction of aliphatic radicals with Ar[•] to form ---CH₂-CH₂-Ar.

Conclusions

Addition of polyolefins in the thermal cracking of heavy oils increased the hydrogen to carbon ratio of the feedstock and therefore improved the distillate yields. Competitive radical interactions reduced the retrogressive reactions and had a significant effect on coke suppression.

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Table 1 - Characteristics of feedstocks

	CLVB	Athabasca Blumen	PE (HDPE)	PP	PS
D1160 Distillation (wt %)					
S25 9C-	16.6	47.6			
S25 9C+	83.2	52.4			
Microcarbon residue (wt %)	17.1	14.3			
Relative density (g/ml.)	1.038	1.013	0.98	0.89	1.06
Elemental analysis (wt %)					
(as received)					
Carbon	78.6	83.3	85.3	85.3	91.9
Hydrogen	9.3	10.9	13.9	14.2	7.7
Nitrogen	0.6	0.6	-	-	-
Sulphur	5.5	4.6	-	-	-
Oxygen	0.9				
V, Ni, Fe (ppm)					
(as received)					
Vanadium	235	197.0			
Nickel	83	74.0			
Iron	18	700.0			

Table 2 - Distribution of products obtained from bitumen
in the presence of PE, PP and PS

Feed wt %					
Athabasca bitumen	100.0	80.0	80.0	80.0	73.0
PE	0.0	20.0	13.5	13.5	20.0
PP	0.0	0.0	6.5	0.0	7.0
PS	0.0	0.0	0.0	6.5	0.0
	Yields wt %				
Distillate	64.3	69.1	62.7	65.8	69.4
THFS	18.1	11.3	12.6	10.5	14.2
THFI	11.0	7.5	7.7	7.7	4.7
Residue:THFS+THFI	27.1	18.8	20.3	18.2	18.9
Gases	5.6	5.8	6.6	7.3	5.5
Total	97.0	93.7	89.6	91.3	83.8
Loss	3.0	6.3	10.4	8.7	6.4
Extra distillate produced by feedstock mixture*	--	4.0	1.7	3.1	1.9

* - Based on distillate from bitumen only: eg. [(69.1+6.3)-(64.3+0.6+20)]

Table 3 - Distribution of products obtained from CLVB in the presence of PE

CLVB wt %	100.0	95.0	90.0	85.0	80.0	70.0	50.0	0.0
PE wt %	0.0	5.0	10.0	15.0	20.0	30.0	50.0	100.0
	Yields wt %							
TS	76.3	78.7	80.3	87.3	87.9	87.9	91.4	97.7
THFS	1.7	4.9	2.3	2.1	0.6	1.4	0.2	0.2
THFI	18.3	14.8	14.0	8.7	8.2	7.3	5.9	1.0
Gases	3.7	3.8	3.4	1.9	3.3	3.4	2.5	1.1

Table 4 - Final pressure at reaction temperature of PE with heavy oils
and hydrogen concentration in gases
Initial pressure: 1atm at room temperature (nitrogen)

PE, wt %	0.0	10.0	15.0	20.0	50.0	100.0
Feed:						
CLVB						
wt %	100.0	90.0	85.0	80.0	50.0	0.0
	Final Pressure					
psi	980.0	950.0	925.0	1080.0	900.0	620.0
Atm	66.8	64.8	63.1	73.6	61.3	42.3
H ₂ wt %*	9.2	9.1	9.2	9.2	6.7	18.3
H ₂ ** consump.	--	1.0	2.3	1.8	7.1	--
Feed:						
Bitumen,						
wt %	100.0	90.0	85.0	80.0	50.0	0.0
	Final Pressure					
psi	1468.0	1417.0	1100.0	887.0	874.0	620.0
MPa	100.1	96.6	75.0	59.1	45.9	42.3
H ₂ wt %*	6.5	6.4	6.4	9.1	12.1	18.3
H ₂ ** consump.	--	1.3	1.9	-0.3	0.3	--

* - Hydrogen concentration in gases

** - Based on 100% polyolefins

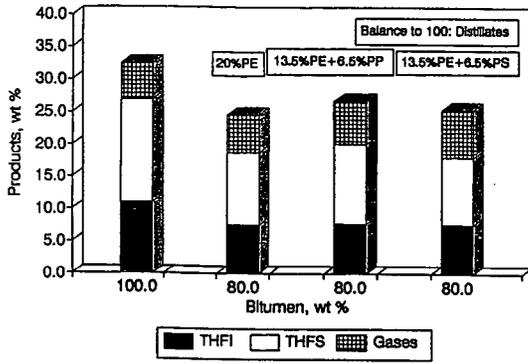


Figure 1. Effect of polyolefin types on products formation from bitumen

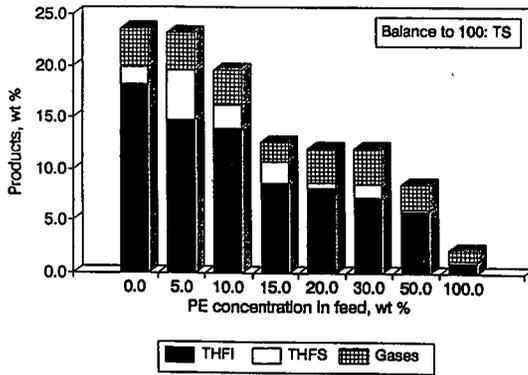


Figure 2. Effect of PE concentration on products formation from CLVB

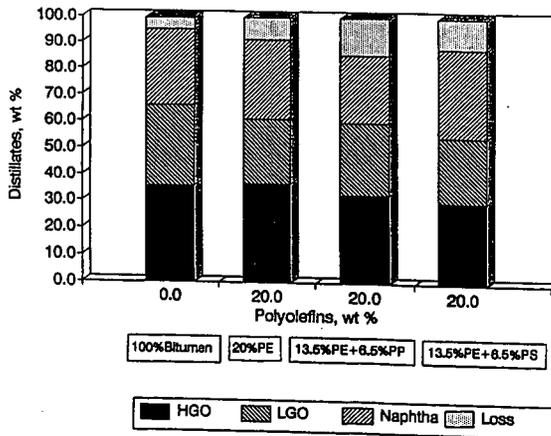


Figure 3 -Effect of polyolefin types on distillates composition from bitumen

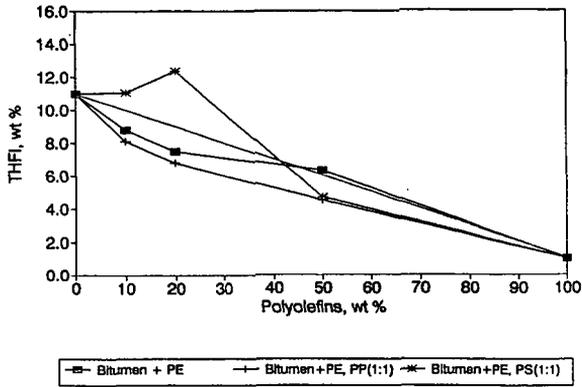


Figure 4 -Effect of polyolefins concentration on coke formation

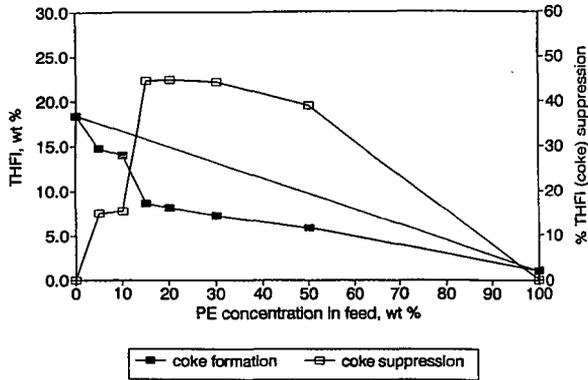


Figure 5 -Effect of PE concentration on suppression of coke from CLVB

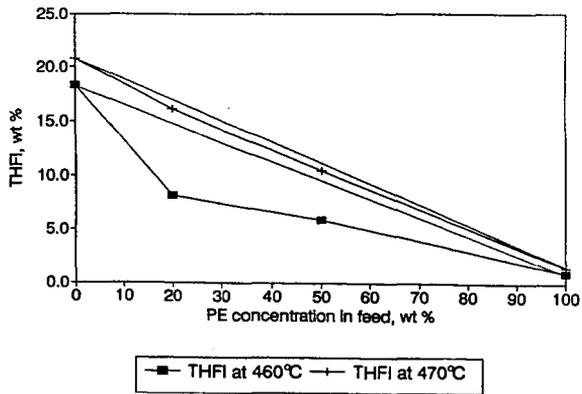


Figure 6 -Effect of temperature on suppression of coke from CLVB

EXTRAHEAVY CRUDE OIL UPGRADING IN THE PRESENCE OF NATURAL GAS AS HYDROGEN SOURCE. CONTINUOUS FLOW EXPERIMENTS AND ECONOMIC EVALUATION
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Key Words: Upgrading, Extraheavy Crude Oil, Methane, Economic Evaluations

INTRODUCTION

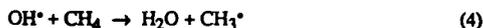
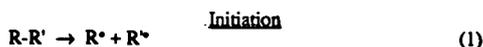
The presence of vast reserves of natural gas available in different parts of the world has motivated continuous research efforts in new routes for the utilization of this raw material [1-8]. Specifically, the direct use of methane as a source of hydrogen for coal and crude oil upgrading has received the attention of several research groups during the last few years [5-8].

Sundaran and coworkers [5] employed natural gas (methane) as hydrogen source for coal liquefaction and found a 73% conversion of a Illinois #6 coal at 425°C and 1000 psi using tetralin as a donor solvent. When employing nitrogen instead of methane, lower conversion was found (67%) indicating that, most probably, methane was involved in the liquefaction process.

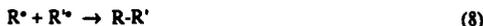
Egiebor and Gray reported [6] 60-70% conversion to liquid products for the liquefaction of Highvale coal using methane atmosphere in the presence or not of a catalyst (Fe₂O₃) with tetralin as a donor solvent at 450°C and a pressure of 270-350 psi. The characterization of the hydrocarbon products by ¹H-NMR showed similar spectra for the hydrogen and methane reactions, and by GC and GC-MS analysis of the donor solvent, methyl and dimethyl substituted products were detected.

Ovalles and coworkers studied [7-8] the upgrading of Orinoco-Belt extraheavy crude oil (Hamaca, API 8.6°) using methane as a source of hydrogen under thermal conditions, in the presence of water as additive. The reaction of Hamaca crude oil (water content 4.4%) with methane at 380°C and 1600 psi for 4 h, led to a decrease in two orders of magnitude in the viscosity of the upgraded product (from 500,000 to 1990 cP at 30°C), a percentage of conversion of the 540°C⁺ fraction of 60% and 11.3% of HDS, with respect to the original crude. Compared to the CH₄-containing experiment, a reaction carried out under nitrogen as an inert gas (control experiment) led to a product with higher viscosity (2600 cP), lower conversion of the heavy fraction (54%) and lower HDS (8.3%). These results indicated [7] that methane was involved in the upgrading reactions and, most probably, was behaving as a source of hydrogen for the thermal processes.

According to the ¹H- and ²D-NMR data [7], the most probable pathway is a radical chain mechanism which involves incorporation of methane to the hydrocarbon molecules via the production of methyl radicals. The proposed mechanism is as follows:



Termination



Where R and R' are hydrocarbons.

Reactions carried out using a dehydrated crude oil (less than 1% of H₂O) under methane and nitrogen atmospheres gave approximately similar results (2400 cP, 45% of conversion and 8% of HDS), indicating that the presence of water is necessary in order to achieve methane incorporation into the upgraded products. The beneficial effects of water in the CH₄-containing upgrading reactions of bitumens can be rationalized by the reaction of OH[•] with methane (eq. 4) with the concomitant production of methyl radicals to continue the chain process [7].

In this paper the upgrading of extraheavy crude oil (Hamaca, API 8.6°) was demonstrated in a continuous flow system using natural gas as a source of hydrogen in the presence of water as additive. The effects of the natural gas pressure (1600, 800 and 200 psi), residence time (30 and 45 min) and percentage of water (10 and 20% w/w) were studied using a 0.11 barrels/day hydrovisbreaking unit modified to use natural gas. From now on, we refer to this process as Methanetreatment for comparative reasons.

Due to the vast reserves of Orinoco Belt extraheavy crude oil and the difficulties in its transportation we evaluate the feasibility of using Methanetreatment for this purpose due to availability of natural gas and low cost energy in the vicinities of the production wells. For these reasons, a conceptual engineering design and an economic evaluation were conducted for a 100 MBPD module. Finally, comparisons with conventional technologies were carried out.

EXPERIMENTAL

The extraheavy crude oil employed in this work came from the Hamaca oil field in the Orinoco Belt and its analysis can be found in Table 1. The percentages of volatile material were determined by the method reported by Ceballo and coworkers [9] using a Hewlett-Packard gas-chromatograph, model 5880. The percentage of conversion of the residue >500°C was defined as:

$$\frac{(\% \text{ of residue } 500^{\circ}\text{C}^+ \text{ in crude oil}) - (\% \text{ of residue } 500^{\circ}\text{C}^+ \text{ in upgraded product})}{(\% \text{ of residue } 500^{\circ}\text{C}^+ \text{ in crude oil})} \times 100$$

The viscosities of the crude oils were measured in a Brookfield apparatus, model RVTDV-II. The water concentrations were determined by the Karl Fisher method according with the ASTM standard test D-1744-83. The composition of the natural gas can be found in Table 1. The Conradson carbon contents were measured by the ASTM standard test D-189.

The upgrading reactions were carried out in a 0.11 barrels/day hydrovisbreaking unit modified to use natural gas. The plant consists of three sections: preheating, reaction and separation zone. In the preheating section, the hydrocarbons, water and natural gas were mixed and heated near the reaction temperature (320°C) at the reaction pressure (1600, 800 or 200 psi). The reaction zone included a coil and a soaker reactors connected in series with a volume of 0.285 and 4.7 liters, respectively. Both reactors were kept at the same temperature (390 and 410°C) during each experiment.

The products of the upgrading reactions were distilled by separating the gases from the liquid using a flash unit at 150°C. The unreacted natural gas was recompressed and recycled with a ratio of 20 to 1 with respect to the purge gas. The liquids were stripped with nitrogen at 150°C and top products were condensed. From the last stream, water and light hydrocarbons were separated and the later compounds were mixed with the bottoms of the stripped unit to obtain the reconstituted crude oil. Mass balances were taken every 10-12 hours without formation of coke in the soaker reactor.

The conceptual engineering designs for Visbreaking, Methanetreatment and Hydrovisbreaking processes as well as for more conventional methods for heavy oil transportation such as Heating and Dilution, were carried out. Technical bases for all alternatives were the same (Crude properties, flowrate, pipelenght, etc.). Investment costs (order of magnitude, 25% contingency and grass root) were estimated using INTEVEP's own database and recent vendor quotations. Operating costs were estimated from INTEVEP's recent experiences in similar projects and from feedback from our operating affiliates.

RESULTS AND DISCUSSION

Upgrading Reactions

The reaction of extraheavy crude oil (API = 8.6°) with 1600 psi of natural gas at 410°C with a concentration of water of 10% w/w and a residence time of 30 min (Table 2, exp. 1), led to an increase in the API gravity from 8.6° to 12° in the upgraded product, a decrease in two orders of magnitude in the viscosity (from 500,000 to 1700 cP at 30°C) and a conversion of the 540°C⁺ residue of 35%, with respect to the original crude. During a 10-days run, mass balances were taken every 12 hours without formation of coke in the soaker reactor after the experiment.

Similar value of viscosity (1990 cP) was obtained [7] using a 300 ml-batch reactor under 1600 psi of methane at 380°C for 4 h. Higher percentage of conversion (60%) was found for

the later run than that in continuous flow experiment and can be attributed to the longer residence time.

An increase in the residence time to 45 min (Table 1, exp. 2) did not further elevate the API gravity of the upgraded reconstituted crude oil. However, the viscosity of the product decreased (1100 cP) and the percentage of conversion of the residue increased (49%) due to the longer residence time. On the other hand, the amount of Conradson carbon in the reconstituted crude oil increased from 16.5 to 18% as the residence time was raised from 30 to 45 min. These results indicate that coke was produced during the crude oil upgrading and is consistent with other thermally upgrading processes as for example Visbreaking and Hydrovisbreaking [10-11].

An experiment (Table 1, exp. 3) carried out with 20 % w/w water concentration led to an upgraded product with slightly better properties (1590 cP, 36% conversion of the 540°C⁺ residue and 16.2% of Conradson carbon) in comparison with those obtained with 10% water content (exp. 1). The effect of water as additive for visbreaking type of reaction is very well known in the literature [12]. Its beneficial properties are attributed to the reduction of coke formation and to its hydrogen donor capabilities [7, 12].

The effect of the pressure of natural gas on the viscosity of the upgraded reconstituted crude oils can be seen in Fig. 1. The reactions were carried out at 390°C with 30 min residence time and the results are the average of 10 h mass balances for up to 30 h. In general, it can be seen that the viscosity of the upgraded product in the temperature range 30-60°C decreased as the natural gas pressure increased. These results indicate the involvement of natural gas during the crude oil upgrading reaction. Possible explanations can be attributed to the need of high pressure in order to carry out the methane activation reactions as shown in eq. 3 and 4.

From these results, it can be concluded that the process of upgrading extraheavy crude oil using natural gas as a source of hydrogen looks as a technically feasible option for the industrialization of these abundant raw materials.

Economic Evaluations

In order to assess the Methanetreatment process as an upgrading technology to be used with transportation purposes, an economic evaluation was conducted. Comparisons with similar processes as Visbreaking and Hydrovisbreaking were made as well as with conventional technologies as Heating and Dilution. The basis for the economic evaluations were as follows:

- 100,000 barrels per day plant located at the Orinoco Oil Belt equipped with a 300 Km oil pipe line from the Orinoco reservoir to the Caribbean Sea.
- The operation costs (for the first trimester 1993 Venezuelan based) included: labor, maintenance, insurance and utilities.
- An evaluation period of 17 years and an interest rate of 10% were considered. Investments and operating cost were estimated on 1993 basis
- A credit was added to the technologies with crude oil upgrading (Visbreaking, Methanetreatment and Hydrovisbreaking).
- Cash flows for the evaluation period were obtained considering the investments and annual balances between operating costs and credits for crude oil upgrading when applicable. Net present value analysis was performed in order to compare the different alternatives.

The results of the study are shown in Table 3. It can be seen that the conventional transport technologies (Heating and Dilution) present the lowest investments (145 and 143 MMUS\$, respectively) and operation costs (11 and 10 MMUS\$) that those calculated for Visbreaking, Methanetreatment and Hydrovisbreaking upgrading processes. Therefore, the present net cost for the first two technologies (216 and 212 MMUS\$) are lower than those found for the later three (246, 255 and 330 MMUS\$).

On the other hand, the visbreaking technology offers the lowest investment, operation cost and present net cost among the crude oil upgrading processes. However, the present net cost for the Methanetreatment is relatively close (255 MMUS\$) to that calculated for the visbreaking (246 MMUS\$), due to the higher credits (higher conversions and lower viscosities of the products) of the former in comparison with the later.

In conclusion, conventional transport technologies of Heating and Dilution have economical advantages over Visbreaking, Methanetreatment and Hydrovisbreaking upgrading processes used for transportation purposes. Between the later three technologies, visbreaking is only slightly more economically attractive than the methanetreatment process.

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Table 1. Analysis of the Hamaca Crude Oil and Composition of the Natural Gas Used for the Upgrading Reactions

Hamaca Crude		Natural Gas	% Molar
API Gravity at 60°F	8.6	Methane	75.4
Asphaltenes (% w/w)	12.5	Carbon dioxide	11.2
Nitrogen (ppm)	7500	Ethane	8.8
Sulfur (%w/w)	3.71	Propane	3.65
Nickel (ppm)	102	Butanes	0.77
Vanadium (ppm)	450	Pentanes ⁺	0.12
% of residue 500°C ⁺	57%	Nitrogen	0.02
Viscosity at 30°C (cP)	500,000	Hydrogen	0.04

Table 2. Effects of the Residence Time and the Percentage of Water on the Properties of the Upgraded Reconstituted Crude Oils.^a

Exp.	Residence time (min) ^b	% H ₂ O (w/w) ^c	^a API	Viscosity at 30°C (cP) ^d	% Conv. Residue ^e (± 1%)	Conradson carbon (% w/w)
Crude	-	-	8.6	500,000	-	13.4
1	30	10	12.0	1700	35	16.5
2	45	10	12.0	1100	49	18.0
3	30	20	11.8	1590	36	16.2

^aThe reactions were carried out in 0.11 barrel/day continuous flow plant at 410°C, 1600 psi of natural gas of final pressure. The results are the average of 12 h mass balances for up to 36 h.

^b Residence time in minutes for the coil and soaker reactors. ^c Percent of water by weight in the feedstock. ^d Values ± 100 cP. ^e Percentage of conversion 500°C⁺ is defined in the experimental section. Percentage of volatile material in the crude oil 54% w/w.

Table 3. Investments and Net Present Value (in million of US\$) for the Technologies Used in the Transportation of Extraheavy Crude Oil^a

Costs	Visbreaking ^b	Methanetreatment ^b	Hydrovisbreaking	Heating	Diluent
Total on-sites	180	244	348	-	-
Total off-sites	127	172	247	-	-
Oil pipe line system	88	86	87	145	143
Total Investment (in 3 years)	395	502	582	145 ^c	143 ^c
Annual Operation Costs	(21)	(23)	(40)	(11)	(10)
Annual Upgrading Credits	46	64	97	-	-
Net Present Value	(246)	(255)	(330)	(216)	(212)

^aFor the basis of the study see text. Calculus based on 1993 US\$ over a 17 years life of the plant.

^bA topping step was added previous to the upgrading reactor.

^cTotal Investment in a two years period.

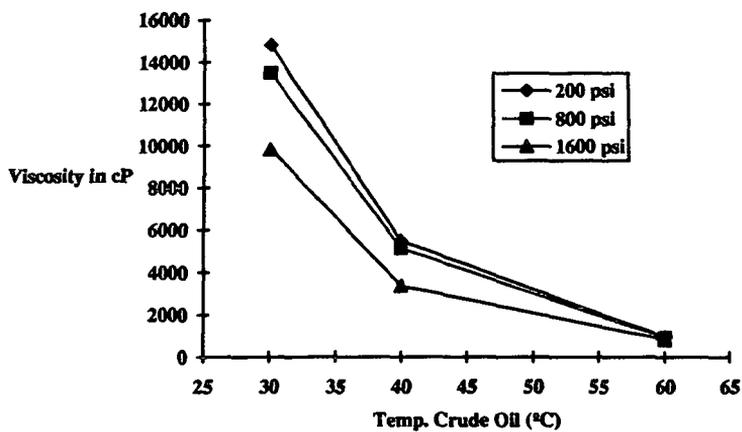


Fig. 1. Effects of the Pressure of Natural Gas on the Viscosity of the Upgraded Reconstituted Crude Oils.

LIGHT OLEFIN PRODUCTION, SKELETAL OLEFIN ISOMERIZATION AND ETHERIFICATION FOR OXYGENATED FUEL PRODUCTION

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Keywords: olefin production; olefin isomerization; SUPERFLEXSM; P,H-ZSM-5; catalytic cracking; MTBE

ARCO's newly developed SUPERFLEXSM process offers opportunities to product high yields of light olefins from a variety of readily available refinery and petrochemical feedstocks. The process is unique in that it employs a catalytic reactor system which is lower in capital and operating costs than conventional steam cracking reactors. The SUPERFLEX process is also more selective for production of propylene and butylenes (including isobutylene) than conventional steam cracking operations. The C₄ product stream from the SUPERFLEX process contains about 20 to 30 percent isobutylene. The SUPERFLEX C₄ product is, therefore, an excellent feedstock for producing MTBE via reaction of the contained isobutylene with methanol. After MTBE production, the isobutylene depleted C₄ stream may be recycled to the SUPERFLEX process to produce additional isobutylene and propylene. This paper will focus on the chemistry and mechanism of catalytic cracking and skeletal olefin isomerization. In addition, there will be some discussion on catalyst activation, life and characterization.

Light Olefin Sources

There are several commercial routes to light olefins. Traditional routes are steam cracking(1), fluid catalytic cracking(2), dehydrogenation(3) and metathesis(4). Recently ARCO Chemical company has developed a new technology known as SUPERFLEXSM which catalytically cracks higher paraffins and olefins in high selectivity to propylene and isobutylene(5). Unlike steam cracking, the propylene to ethylene ratio is high. In addition the butylenes and pentenes are isomerized to their thermodynamic distribution. This technology offers an alternate, low capital route to light olefins. It may be readily integrated into an olefins plant or refinery. Its scale-up is simplified by its analogy to the FCC process. Analogies in operating conditions are given in Table I.

SuperflexSM Technology

The SUPERFLEXSM technology has been demonstrated with olefin plant and refinery streams and with pure components such as isobutylene, butene-1, isopentane, n-pentane, cyclopentane and octane. An integrated pilot unit designed to simulate commercial operation has operated for two years. During this operation catalyst life was confirmed under simulated commercial operation, including recycle. In addition the catalyst was produced on commercial scale. Catalytic activity is sufficient to approach olefin equilibrium in 5 to 15 seconds. Selectivity to aromatics and paraffins is minimal. Catalyst attrition is low with less than 15 wt % loss on the 5 to 15 hour portion of the ASTM D-32.02 TG 06 Jet Attrition Test. Catalyst hydrothermal stability is good with less than 1% activity loss per day. The active catalyst component is a modified ZSM-5. It is formulated into a fluidizable catalyst by combining it with a matrix of silica and kaolin and spray drying. The catalyst working environment is given in Figure 1.

Catalyst Evaluation

Numerous zeolites were synthesized, characterized and evaluated in catalytic cracking reactions to light olefins. H-ZSM-5 was found to be most active and selective. Others of noteworthy activity are listed in Table II. The Si/Al ratio of H-ZSM-5 was varied from 20 to 100. A ratio of approximately 40 was found to be optimal. An inexpensive, non-template H-ZSM-5 performed similar to that of a template one.

Catalyst evaluations were run with 60 to 100 mesh fixed beds consisting of active catalyst diluted in alpha alumina to adjust conversion to reasonable levels. The beds were held in quartz reactors of 6.5 mm i.d. containing a 2 mm o.d. thermowell. Bed lengths were typically 4 cm and bed volumes 1.4 ml. Results were obtained at 550 to 600 °C and 1 atm total pressure. The WHSVs are with respect to the active component of the bed (not including diluent alumina).

Hydrothermal Stability

Resistance to steam deactivation is important for catalyst performance and life since commercial catalytic cracking units operate in the presence of steam and steam is generated in-situ during coke burn-off. Hydrothermal treatment of a catalyst containing H-ZSM-5 with no modifiers caused a two-fold decrease in catalyst activity. Numerous modifiers were evaluated of which phosphorous was most successful. Hydrothermal treatment of a catalyst containing P,H-ZSM-5 increased 2-butene cracking activity fourfold. Deactivation was not evident with subsequent hydrothermal treatments and time on stream. In fact, to maintain high activity continuous or intermittent exposure to steam was necessary. Initial activation of fresh catalyst required more severe steaming at 1100 °F and 1 to 2 atm for 1 to 2 days. Steam pressures of 0.02 to 1 atm were adequate for activity maintenance. A weight loading study indicated the optimal phosphorous loading was close to 1 wt %. Phosphorous was most readily added to the H-ZSM-5 or matrix containing H-ZSM-5 by incipient wetness impregnation with phosphoric acid followed by drying at 120 °C and calcining at 600 °C for 2 hrs. The hydrothermal activation studies are given in Table III and the effect of steam in the feed is given in Table IV.

Characterization of H-ZSM-5 and P,H-ZSM-5

^{27}Al and ^{29}Si MAS NMR of H-ZSM-5 indicated that silicon was in a highly silicious environment typical of H-ZSM-5 for both the fresh and steamed samples. Steaming resulted in fine structure typical of dealumination(6). Aluminum was tetrahedrally coordinated within the zeolitic framework. With steaming, dealumination was evident. There was a decrease in signal intensity for zeolitic aluminum. Non-framework octahedral aluminum became evident(7).

^{27}Al , ^{31}P and ^{29}Si MAS NMR of P,H-ZSM-5 indicated phosphorous was bound to the framework and dealumination had occurred with phosphorous incorporation. With severe steaming phosphorous remained bound to the framework and further dealumination was evident. Silicon remained in a highly silicious environment typical of H-ZSM-5 with phosphorous addition and steaming. Once steamed and equilibrated no further dealumination was evident.

A mechanism for phosphorous bonding to the zeolite framework is given in Figure 2. Phosphorous converts strong Bronsted acid sites into weak ones. On doing so, the pore radius decreases and the geometry at the acid site is altered. Further reaction results in dealumination with AlPO_4 formation.

A constraint index experiment on P,H-ZSM-5 suggested phosphorous was blocking the channels and that catalysis was occurring at the pore mouth and external surface. Using literature procedures (8) the P,H-ZSM-5 gave a constraint index of < 1 whereas, the unmodified H-ZSM-5 gave a constraint index of 10.8. The low constraint index for the phosphorous modified H-ZSM-5 indicated the zeolite no longer discriminated between linear and branched hydrocarbon feed. This was largely attributed to the fact that nearly all reactivity occurred external to the channels. In a separate study a phosphorous modified H-ZSM-5 was analyzed by high resolution electron microscopy (9). In this study it was likewise concluded that phosphorous was blocking the zeolite channels.

Mechanistic Studies

Compared to steam cracking and FCC technology, the SUPERFLEXSM process is best conducted at higher space velocities and temperatures ranging from 550 to 625 °C. Best results are obtained under diffusional limiting conditions under which the majority of the chemistry occurs at the pore mouth where super acid sites are available. For butene conversion the reaction is bimolecular. Two molecules of butene react to give octene which subsequently disproportionates to olefins, alkanes and aromatics. See Figure 3. A second order rate constant of $1.1 \times 10^7 \text{ cm}^3/\text{mole sec}$ has been experimentally determined. Little or no diffusion into the pore occurs since the rate of diffusion is much slower, less than or equal to $1 \times 10^{-8} \text{ cm}^2/\text{sec}$. (10).

n-Butene Skeletal Isomerization

A major objective was to integrate skeletal isomerization with SUPERFLEXSM to make more isobutylene and isoamylene for MTBE and TAME production. By adjusting reaction conditions skeletal isomerization could be conducted successfully over the SUPERFLEXSM catalyst. Higher temperatures, 625-650 °C vs. 550-625 °C, favored isomerization over cracking. This is largely due to the fact that cracking is a bimolecular process requiring longer surface residence time. Whereas the skeletal isomerization is a

uni-molecular process. By a similar argument, increased pressure favored cracking. Due to the fact that steam generates more Bronsted acid sites, under these conditions cracking was favored. Whereas, with no steam, Lewis acid sites predominated and skeletal isomerization was favored. Iso-olefin selectivities increased with gas velocity due to increased mass transfer rates.

The SUPERFLEXSM catalyst ran in a pilot fluid bed unit and gave 15% isobutylene yield under optimal isomerization conditions while meeting productivity, life, attrition and cost targets. Results from the lab and pilot unit are given in Table V. In addition, a catalyst consisting of Mg-APSO-31 was found to be effective for skeletal isomerization (11). It was more selective than the SUPERFLEXSM catalyst due to lower acidity yet was lower in activity and more expensive. See Table V for results.

Etherification

A process scheme for converting the iso-olefins produced from an isomerization unit to ethers was proposed and patented (12). The process scheme could potentially utilize the approximately 350,000 BBL/day of C₅⁼ olefins produced at U.S. refineries. The combined mole fraction of 2-methyl-2-butene and 2-methyl-1-butene at equilibrium exceeds 0.80 at 300 °F. These olefins may be converted to TAA and/or TAME.

Conclusions

A new technology for producing light olefins in high yields has been developed which uses a phosphorous modified H-ZSM-5. The catalyst has been extensively evaluated in a pilot unit and found to withstand hydrothermal and attrition testing. By modifying the reaction conditions skeletal olefin isomerization may be conducted with the same catalyst. Finally, an iso-olefin etherification step may be carried out for oxygenated fuel production.

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TABLE I
SUPERFLEX PROCESS
COMPARISON WITH FLUID CATALYTIC CRACKING

	SUPERFLEX DESIGN	FCC
Coke Yield, Wt %	< 1	3 to 7
Riser Temp., °C	550 to 650	500 to 550
Regen Temp., °C	625 to 725	675 to 775
Feed	C_4 to C_{10}	Gas Oil (C_{12}^{**})
Cat/Oil, Wt	12 to 25	5 to 8
Catalyst Make-Up Rate, %/day	1.0 to 2.5	1.0 to 2.0

TABLE II
2-BUTENE CONVERSION

Catalyst	Temp °C	WHSV hr ⁻¹	% C_4^{+} Conv	% Selectivity					
				C_3^{+}	C_2^{+}	C1-4	C5,6	Coke	BD
H-ZSM-5 (HCl Prep)	550	833	68.9	50.6	11.2	10.9	27.0	0.2	0.2
H-ZSM-5 (NH_4 Cl Prep)	550	833	68.9	45.8	7.9	9.7	35.9	0.6	0.2
H-ZSM-11	550	833	30.8	36.4	1.1	6.1	56.5	0.01	0.2
Beta	600	550	56.4	20.8	2.5	11.8	64.7	0.3	0.2
Zeolite Y	600	275	58.4	31.7	3.8	20.2	41.6	2.6	0.1
Mordenite	600	275	54.2	43.3	9.4	21.6	22.9	2.6	0.3
USY	550	124	64.9	28.1	3.5	38.9	29.5	2.8	0.09
H-ZSM-34	550	55	58.0	42.0	15.0	16.5	16.1	10.1	0.2
Omega	600	55	37.1	43.7	5.7	16.0	34.1	0.4	0.6
Matrix (Aluminosilicate)	600	6.9	9.4	23.7	4.1	20.6	27.7	0.9	23.9
α - Al_2O_3	600	14	5.6	5.8	0.8	82.9	9.1	1.5	0.7

TABLE III

2 - BUTENE CONVERSION

EFFECT OF PHOSPHORUS AND STEAM ON H-ZSM-5

	1% P,H-ZSM-5, Prior to Hydrothermal Activation	1% P,H-ZSM-5, After Hydrothermal Activation	H-ZSM-5 Prior to Hydrothermal Activation	H-ZSM-5 After Hydrothermal Activation
Temp., °C	600	600	600	600
WHSV, HR ⁻¹	31	125	62.5	31
% C ₄ ^a Conv.	60	65	57	59
% Sel to:				
CH ₄	0.21	0.11	0.91	1.30
C ₂	0.12	0.09	0.19	0.31
C ₃ ^a	11.20	8.70	14.20	18.00
C ₃	1.10	1.40	1.60	1.80
C ₅ ^a	49.00	49.90	52.00	55.70
Isobutane	2.00	1.80	3.30	3.30
N-Butane	6.40	5.80	5.10	4.50
Butadiene	0.33	0.26	0.27	0.31
C ₅	17.40	18.10	14.60	9.40
C ₆	12.10	23.80	7.90	5.40
Coke	0.20	0.06	0.11	0.44

TABLE IV

ONCE-THROUGH LAB RUNS OF 2-BUTENE OVER COMMERCIALY
VIALE SUPERFLEX CATALYST AT 600°C (1110°F)

	A	B	C	D	E	F	G
Catalyst History	Fresh	Fresh	Used 12 Days in Pilot Unit	As In C	As In C	As In C	As In C
Steam	None	Before Run 550°C, 2 atm 24 Hrs	In Regenerator 620°C, 0.2 atm, 5 Cycles/Hr	As In C, Then 2 Dry Cycles	As In D, Then 500°C, 0.5 atm, 2 Hrs	As In D, Then 600°C, 0.03 atm, 20 Sec	As In D, Then 0.1 atm in Butene and Regeneration
WHSV	65	93	65	65	130	65	70
% Butene Conversion	25	60	75	60	65	71	64
% Selectivity To:							
CH ₄	0.2	0.2	0.2	0.2	0.1	0.1	0.2
C ₂ H ₆	8	16	20	13	12	14	12
C ₃ H ₆	0.1	0.2	0.3	0.7	0.1	0.2	0.1
C ₃ H ₈	41	55	53	57	53	53	59
C ₄ H ₆	0.2	1.9	3.1	1.4	2.6	2.4	1.9
C ₄ H ₈	0.8	0.2	0.4	0.2	0.1	0.2	0.2
C ₄ H ₁₀	16	8.7	8.1	8.7	8.8	8.8	8.2
C ₅	30	11	7	14	14	12	13
C ₆	8	7	7	5	8	8	5
COKE	1.7	0.2	0.4	0.6	0.2	0.1	0.1

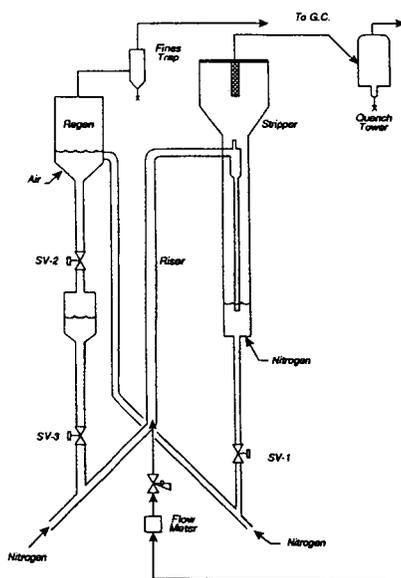
TABLE V

n-C₄= SKELETAL ISOMERIZATION

	<u>SUPERFLEX Catalyst</u>		<u>Mg-APSO-31</u>
	<u>PILOT</u>	<u>LAB</u>	<u>LAB</u>
λ YIELD %	15	19	30
λ SELECTIVITY %	25	47	80
<i>n</i> -C ₄ = CONVERSION %	60	41	38
TEMPERATURE, °C	650	625	575
WHSV, hr ⁻¹	250	296	46
LIFE	GOOD	---	TO BE DETERMINED
FLUIDITY	GOOD	---	ACTIVITY TOO LOW
ATTRITION RESISTANCE	5-7%		PROBABLY GOOD

FIGURE 1

CATALYST WORKING ENVIRONMENT



	<u>Reactor</u>	<u>Stripper</u>	<u>Regenerator</u>
Temp, °C	550 - 650	550 - 650	550 - 650
Residence Time	2 to 6 secs	4 to 5 min	4 to 6 min
% Steam	Negl.	25 to 50	5 to 20

FIGURE 2

**Mechanism for Phosphorous Bonding
to the Zeolite Framework**

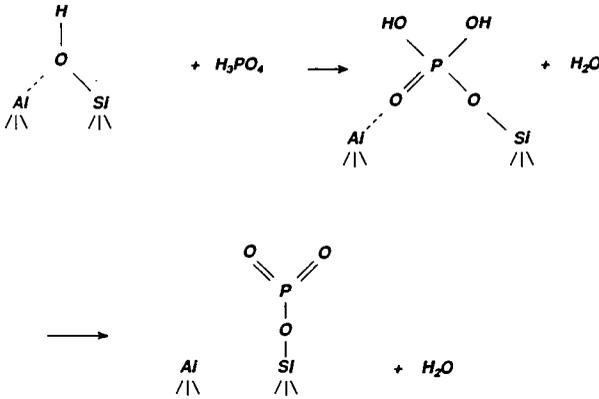
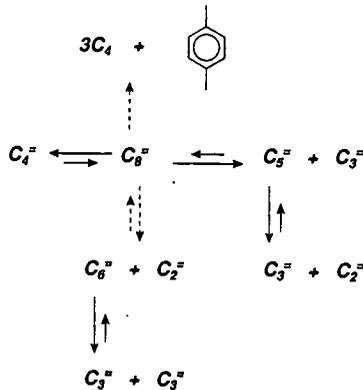


FIGURE 3

MECHANISM



SHAPE-SELECTIVE ISOPROPYLATION OF NAPHTHALENE OVER DEALUMINATED MORDENITES

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Keywords: naphthalene, shape-selective alkylation, zeolite

INTRODUCTION

In effort to enhance the economic feasibility of coal liquefaction we are continuing the investigation of non-fuel applications for coal-derived liquids (CDL). Conversion of a small fraction of the naphthalene can significantly increase value, while the majority of the CDL is used as transportation fuel. This study is aimed at the regioselective alkylation of naphthalene. Of particular interest is 2,6-diisopropyl-naphthalene (2,6-DIPN) that, when oxidized to the corresponding diacid, can be polymerized to produce high-value engineering plastics and liquid crystalline polymers.¹ Mordenites having high selectivity for 2,6-DIPN production have been reported in a patent by Fellmann et al. at Catalytica, Inc.² However, fundamentals of the alkylation process are poorly understood.

Our research is directed at optimizing 2,6-DIPN selectivity through control of reaction parameters. Effects of temperature, identity of the alkylating agent, naphthalene to catalyst ratio, and addition of water are discussed. An understanding of catalyst physical and chemical properties is pertinent to the design of shape-selective catalysts. Beyond chemical analysis, X-ray powder diffraction has been used to measure crystallinity, cell constants, and crystallite size.

EXPERIMENTAL

Materials. All chemicals were used as supplied. Naphthalene (99 %) and isopropyl alcohol (99.5+ %) were obtained from Aldrich Chemical, Inc. 2,6-Diisopropyl-naphthalene (GR) was obtained from TCI, Ltd. Propylene (99.5 % minimum, *polymer purity*) was obtained from Matheson, Inc. and delivered to the reactor in vapor form.

Catalysts. Sodium and hydrogen mordenites were supplied as 9-10 μm average particle size powders (The PQ Corporation, Inc.). Properties of these materials are listed in Table 1. The H-form of NaM14 was obtained by sodium-exchange with 1 M NH_4Cl , followed by wash, dry and calcine procedures. Dealumination of HM14 was accomplished by stirring in aqueous hydrochloric or nitric acid at reflux temperature. Time and acid concentration were varied to control the extent of aluminum removal as summarized in Table 2. Following the acid treatment, the catalysts were washed extensively with hot deionized water, dried, and calcined (5.5 h at 465 °C unless otherwise specified). Samples were dissolved using lithium metaborate fusion and analyzed for silicon, aluminum and sodium by ICP-AES.

Catalyst Evaluation. A 30 cm^3 , stainless-steel tubing bomb, batch reactor was used for all experiments. The standard reactor charge was 0.10 g catalyst, 1.0 g (7.8 mmol) naphthalene, and 0.66 g (15.6 mmol) propylene. For runs with added deionized water, the catalyst amount was increased to 0.15 g. The reactor was mounted on a holder and immersed in a fluidized sand-bath heater. During the run, the reactor was agitated at 3.3 cps. Test conditions were typically a 2 h run at 200 °C. At the end of the test, the reaction was quenched in cold water. The reaction products were collected in acetone solution and analyzed by GC-MS and GC-FID for qualitative and quantitative analyses, respectively. The GC column was 30 m x 0.25 mm DB-17 (J&W Scientific).

RESULTS AND DISCUSSION

Catalysis Test Results. Activity, selectivity and regioselectivity are compared in Table 3 for all of the catalysts in 2 h runs at 200 °C. HM110 and HM230 were run both 2 and 4 h, at 200, 250 and 275 °C. The first five lines of Table 3 detail the results for dealumination of HM14, while the other tests refer to HM38, and HM54 and its dealumination. Isopropyl-substituted naphthalenes (IPN's) constituted 95-99+ % of the products. The major side products were alkyl-substituted naphthalenes (RNAP's) other than *solely* isopropyl-substituted naphthalenes. Disproportionation of IPN's and reaction between naphthalene and propylene dimer (or oligomer) are likely the main sources for RNAP's. Mass balances of less 100 % were primarily due to material loss as carbonaceous deposits on the catalysts, and to a lesser extent, uncharacterized minor products.

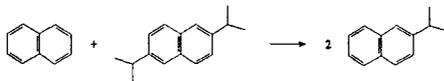
Comparing the 2 h/200 °C data, naphthalene conversion increases slightly or remains unchanged with mild dealumination, but decreases markedly at higher levels of dealumination. HM230 shows higher activity than what is predicted by the trend observed for HM70-HM110, but this may be due to structural changes as discussed below. Similar volcano plots of activity vs. $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio have been reported for reactions of aromatics over mordenites.^{3,4} One explanation for this behavior involves the number and nature of acid sites. Acid site density decreases, and acid

strength increases, with aluminum removal leading to an increase in activity. Ultimately, activity is suppressed by gross depletion of acid sites at high levels of dealumination. Other justifications focus on factors that effect diffusion: changes in mesopore volume, changes in channel structure and dimensions (or channel collapse at high levels of dealumination), and differing rates of fouling. Regardless, the height and position of the activity maximum is dependent upon the reactant, reaction conditions and catalyst preparation.³

Dealumination increases the regioselectivity for β -alkylation (% β -alkylation): % 2-isomer in the monoisopropyl (MIPN) product and % 2,6-isomer in the diisopropyl (DIPN) product both increase. Third (TRIPN) and fourth (TEIPN) isopropylations are also generally diminished, substantially in some cases. Changes in the polyalkylated product with dealumination are nicely illustrated in Figure 1(a)-(c). The larger unlabeled peaks on either side of 2,7- and 2,6-DIPN are isomeric DIPN's. There are ten possible isomers. Fellmann et al. have observed similar changes in DIPN and TRIPN+ distributions with dealumination.² The main DIPN products are the 2,6- and 2,7-isomers. Non-selective catalysts produce nearly equal amounts of these isomers.^{2,5} As observed here and elsewhere,^{2,6,7} the 2,6/2,7 ratio greatly exceeds unity for shape-selective catalysts. It has been suggested by Song et al. that 2,6-DIPN is slightly smaller and may diffuse more rapidly than 2,7-DIPN.⁷ Interestingly, the 2,6/2,7 ratio reaches a maximum at $\text{SiO}_2/\text{Al}_2\text{O}_3$ ca. 71 for 200 °C runs, even though % β -alkylation continues to increase at higher dealumination levels.

Alkylation regioselectivity depends on the nature of the catalyst, catalyst charge, temperature, time and water content. Typically, % 2- in MIPN does not exceed 90% unless the catalyst and reaction conditions are optimized.^{2,5,8} For naphthalene substitution by isopropyl bromide over mordenite at 200 °C, Moreau et al. report nearly 100 % selectivity for the 2-isomer in the MIPN product.⁵ They used a naphthalene/catalyst (N/C) mass ratio of 0.64. We tested HM38 with N/C = 0.62 at 200 °C, and compared the results with our standard run conditions (N/C = 10) at comparable conversion. As shown in Table 4, decreasing N/C dramatically increases % β -alkylation. However, there is a concurrent 11 % decrease in the 2,6/2,7 ratio.

At 25 °C, the equilibrium MIPN isomer distribution is 98.5 % 2-isomer.⁹ Substitution at the more active α -positions of naphthalene leads to the kinetic product. Fellmann et al. obtained the following equilibrium product distribution over amorphous $\text{SiO}_2\text{-Al}_2\text{O}_3$ at 275 °C: 37 % 2,6- in DIPN with 2,6/2,7 of 1.0. Our results for N/C = 0.62 follow the trends discussed by Fellmann et al. with N/C = 90. Conversion increases, while both the % 2,6- in DIPN and the 2,6/2,7 ratio decrease over time. These changes are apparently equilibrium driven. Whereas Fellmann et al. do not comment on changes in the MIPN isomer ratio, we observe an increase in the relative amount of the 2-isomer with time. This may be due to either a higher rate for 1-MIPN \rightarrow 2-MIPN isomerization than for alkylation of 2-MIPN, or transalkylation between 2,6-DIPN and naphthalene.



With N/C = 10, there simply are not enough appropriate acid sites available for rapid isomerization of the kinetic 1-MIPN product. The %2- in MIPN is low, and consecutive alkylation does not give a DIPN product distribution enriched in the 2,6-isomer. From Table 3 (N/C = 10), conversion increases with time over HM110 and HM230, while % β -alkylation and the 2,6/2,7 ratio remain approximately constant with time. Although not shown here, the same trends were observed for HM38 with N/C = 10.

Increasing the reaction temperature to 250 or 275 °C (Table 3) causes a substantial increase in conversion. The 2,6/2,7 ratio increases markedly, and % β -alkylation is mildly increased. It may be concluded that 2,6-DIPN is thermodynamically more stable, and 2,7-DIPN is the kinetic product.

In separate experiments, we examined the fate of 2,6-DIPN over three mordenites in 2 h, 200 °C reactions. Table 5 shows that the principle reaction is alkylation. At low propylene pressure, isomerization does occur over HM14 and HM38, principally to DIPN isomers other than 2,7-DIPN. Higher propylene pressures retard isomerization—an effect also demonstrated in propylene addition to biphenyl.¹⁰ Dealuminated mordenite, HM74, gives almost no isomerization. The % 2,6-DIPN remains high, while other DIPN isomers react to form higher alkylates. Over aluminum-deficient mordenites, 2,6-DIPN is apparently less reactive toward alkylation than other DIPN isomers. This is not the case for HM14 and HM38 where 10-30 % of 2,6-DIPN is converted, mostly to higher alkylates. Structural analysis of the TRIPN isomeric products, from isotopically labeled DIPN if necessary, would aid the interpretation of these results.

In related work on the isopropylation of naphthalene over HM38 and other zeolites, we have observed higher β -alkylation selectivities and higher 2,6/2,7 ratios for isopropyl alcohol, rather than propylene addition.⁷ Byproduct water is inherent when alcohols are used. To test the hypothesis that the presence of water enhances regioselectivity, a series of experiments were performed where the amount of catalyst, naphthalene, and propylene in the reactor were held constant. Water was added

in various amounts. Catalyst mass in the reactor was increased to 0.15 g for these experiments to amplify the changes brought about by water addition. Changes in the polyalkylated product distribution with added water are illustrated in Figure 1(d)-(f) and Table 6. A small amount of water poisons the catalyst, but larger amounts bolster activity up to an apparent saturation limit. The maximum in activity is approximately at 160 mg added water—very close to the mass of catalyst in the reactor. A possible explanation is that at low partial pressures, water adsorbs on catalytic acid-sites and impairs adsorption of reactants. Higher partial pressures of water lead to the genesis of new Brønsted acid catalytic sites, leading to higher conversion. Ultimately, high moisture levels reduce conversion due to impeded reactant diffusion. This proposition may also explain the increase in β -alkylation selectivity and 2,6/2,7 ratio with added water. Adsorption of water impedes reaction on the non-selective external surface of the catalyst. A higher percentage of the naphthalene molecules react within the shape-selective confines of the mordenite channels. Adsorption of water within the mordenite channels impedes diffusion. More so in the case of the larger α -, α,β -, and α,α -substituted products. The result again is higher % β -alkylation. It is unclear why the 2,6/2,7 ratio drops sharply above 160 mg added water, even though % β -alkylation does not. However, throughout this work there is a positive correlation between the 2,6/2,7 ratio and conversion. Our preliminary data show that the regioselectivity enhancement resulting from added water is even more pronounced for less shape-selective mordenites.

Catalyst Characterization by XRD. Four of the catalysts have been examined by XRD (Cu K α radiation): HM14, HM74, HM110 and HM230. Overall, XRD shows that dealumination following calcination at 700 °C causes a partial structure collapse that is not observed for samples calcined at 465 °C. Estimates of mean crystallite dimension were made using the Scherrer equation, assuming Cauchy profiles. Average results for measurements on the six strongest, well-resolved reflections are reported here. Natural sodalite was used as a standard for instrumental line broadening. Within error of measurement, HM14, HM74 and HM110 are of the same crystallite size, 230 \pm 20 nm. However, HM230 crystallites are smaller, 140 \pm 10 nm.

Comparison of the area sum for the six peaks allows an estimate of relative crystallinity. HM230 is approximately only two-thirds crystalline material; whereas, the other three samples are of the same relative crystallinity (assumed 100%).

Least-squares regression analyses were used to obtain precision measurements of the cell constants from the diffraction data. It is only possible to compare relative differences between the samples at this time (see Figure 2), since the data have not been zero- nor background-corrected. As summarized by Mishin et al., dealumination of mordenites results in a lattice contraction that is generally anisotropic.³ Our data show that changes in the a-dimension are the largest. Decreases in b and c are similar, but smaller than for a. HM230 showed the largest magnitude lattice contraction. HM74 and HM110 show the same overall cell volume decrease. The contraction is isotropic for HM74; whereas, for HM110 and HM230, it is not.

CONCLUSIONS

We have succeeded in identifying several important parameters that govern selectivity in the addition of propylene to naphthalene. The naphthalene/catalyst ratio (N/C) has significant impact on the resulting β -alkylation selectivity. For a given N/C, the 2,6/2,7 ratio closely parallels naphthalene conversion. Yield of 2,6-DIPN was inherently higher for N/C = 0.62, but both % 2,6- in DIPN, and the 2,6/2,7 DIPN isomer ratio decrease over time. Increasing N/C to 10 requires shape-selective dealuminated mordenites and reaction temperatures in excess of 200 °C to obtain good 2,6-DIPN yields. Longer reaction times increase conversion and DIPN yield, while MIPN and DIPN isomer distributions do not change. The 2,6/2,7 ratio increases with temperature, indicating that 2,6-DIPN is thermodynamically more stable. With N/C = 10, 2,6-DIPN is neither isomerized nor alkylated to any appreciable extent over high-silica mordenites. We have also found that addition of water to the reactor, in amounts up to approximately the mass of catalyst, results in substantial gains in regioselectivity.

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Table 1. Properties of the Mordenite Starting Materials¹

catalyst	SiO ₂ /Al ₂ O ₃ , molar	Na ₂ O, wt %	surface area, m ² /g	porosity, cm ³ /g	
				meso ²	micro ³
NaM14	14.3	6.24	466	0.14	0.17
HM38	37.5	0.07	512	0.13	0.17

¹Data as reported by the supplier. ²Meso refers to 20-600 Å pores. ³Micro refers to < 20 Å pores.

Table 2. Preparation and Composition of Mordenite Catalysts Used in This Work

catalyst	treatment ¹	SiO ₂ /Al ₂ O ₃ ,	Na ₂ O,
		molar	wt %
HM14	exchange NaM14 with 1 M NH ₄ Cl	13	0.19
HM54	stir NaM14 in 1 M HCl for 24 h at reflux	54	0.15
HM70	stir HM14 in 1 M HCl for 5 h at reflux	70	< 0.01
HM71	stir HM14 in 1 M HCl for 10 h at reflux	71	< 0.01
HM74	stir HM14 in 1 M HCl for 24 h at reflux	74	< 0.01
HM90	stir HM14 in 3 M HCl for 24 h at reflux	90	< 0.01
HM110	calcine HM54 at 465 °C, then stir product in 6 M HNO ₃ for 24 h at reflux. Final calcination at 465 °C.	110	< 0.01
HM230	calcine HM54 at 700 °C, then stir product in 6 M HNO ₃ for 24 h at reflux. Final calcination at 700 °C.	230	< 0.01

¹All catalysts calcined 5.5 h at 465 °C unless otherwise specified.

Table 3. Results for Propylene Addition to Naphthalene¹

catalyst	T, °C	time, h	%NAP conv	product distribution, molar basis							
				% yield		% MIPN	% DIPN	% TRIPN+ in MIPN	% 2- in DIPN	% 2,6- in DIPN	2,6/2,7 ratio
				IPN's	RNAP's						
HM14	200	2	76	67	0.9	64	33	3.6	60	33	1.76
HM70	200	2	83	69	1.4	53	41	5.7	59	44	2.17
HM71	200	2	74	65	1.2	61	37	2.3	64	51	2.29
HM74	200	2	47	41	0.5	76	23	0.6	71	55	2.24
HM90	200	2	36	32	0.3	80	19	0.9	70	53	2.21
HM38	200	2	73	61	1.0	61	34	4.5	58	39	1.99
HM54	200	2	43	41	0.6	76	23	1.2	68	50	2.11
HM110	200	2	15	16	0.2	85	15	0.4	83	61	2.05
HM110	250	2	28	28	0.6	79	21	0.6	86	65	2.48
HM110	275	2	46	42	1.5	71	28	1.0	87	66	2.67
HM110	200	4	19	19	0.3	83	17	0.4	83	61	2.09
HM110	250	4	39	36	1.1	75	25	0.7	86	65	2.48
HM110	275	4	58	51	2.3	66	33	1.3	87	65	2.64
HM230	200	2	41	40	0.8	74	25	1.1	74	58	2.32
HM230	250	2	63	58	1.2	59	39	2.3	78	62	2.57
HM230	275	2	76	67	1.6	49	47	4.0	79	62	2.58
HM230	200	4	49	46	0.9	70	29	1.2	73	59	2.37
HM230	250	4	75	68	1.7	50	46	4.3	75	60	2.51
HM230	275	4	84	74	1.9	41	54	4.4	78	62	2.54

¹Catalyst charge 0.10 g.

Table 4. Comparison of HM38 Using Different Naphthalene to Catalyst Ratios at 200 °C

reactor charge	%NAP conv	product distribution, molar basis							
		% yield		% MIPN	% DIPN	% TRIPN+	% 2- in MIPN	% 2,6- in DIPN	2,6/2,7 ratio
		IPN's	RNAP's						
1.00 g naphthalene and 0.10 g HM38	90	75	1.1	46	46	7.2	53	38	2.06
0.62 g naphthalene and 1.00 g HM38	88	67	2.5	51	46	3.4	90	52	1.85

Table 5. Reaction of 2,6-Diisopropylnaphthalene Over Mordenites in 2 h, 200 °C Runs¹

catalyst	propylene/ 2,6-DIPN, molar	product distribution, molar basis						
		% MIPN	% 2,6-DIPN	% 2,7-DIPN	% other DIPN	% TRIPN	% TEIPN	% RNAP
none start. mat'l.	—	3.48	95.46	0.39	0.31	0.17	0.00	0.19
HM14	4.0	0.00	69.58	0.09	0.26	26.06	3.67	0.33
HM14	1.0	0.11	71.18	0.29	1.93	23.40	2.77	0.32
HM14	0.5	0.43	72.61	1.06	4.57	19.09	1.93	0.31
HM38	4.0	0.19	71.59	0.11	0.29	24.92	2.73	0.17
HM38	1.0	2.22	73.65	0.20	1.15	19.61	1.93	1.25
HM38	0.5	0.12	83.54	0.21	1.25	13.44	1.18	0.25
HM74	4.0	0.00	94.72	0.07	0.09	4.42	0.46	0.24
HM74	1.0	0.01	96.67	0.08	0.13	2.58	0.26	0.26
HM74	0.5	0.00	96.87	0.09	0.22	2.35	0.23	0.25

¹ Reactor charge: 1.00 g (4.71 mmol) 2,6-diisopropylnaphthalene, 0.10 g catalyst, and varied propylene pressure.

Table 6. Propylene Addition to Naphthalene Over HM74 in 2 h, 200 °C Runs with Various Amounts of Added Water¹

added water, mg	%NAP conv	product distribution (molar basis)							
		% yield		% MIPN	% DIPN	% TRIPN+	% 2- in MIPN	% 2,6- in DIPN	2,6/2,7 ratio
		IPN's	RNAP's						
0	56	51	1.2	69	29	1.7	67	53	2.24
10	40	38	0.7	77	23	0.7	75	59	2.22
40	33	32	0.6	79	21	0.6	80	64	2.37
50	29	28	0.6	77	23	0.8	80	63	2.38
100	45	42	0.9	75	25	0.5	84	68	2.61
120	54	52	1.2	73	27	0.5	84	69	2.62
120	55	51	1.2	72	28	0.5	84	69	2.65
160	59	54	1.4	72	28	0.4	84	68	2.56
300	22	22	0.3	88	12	0.1	86	66	2.15

¹ Catalyst charge 0.15 g.

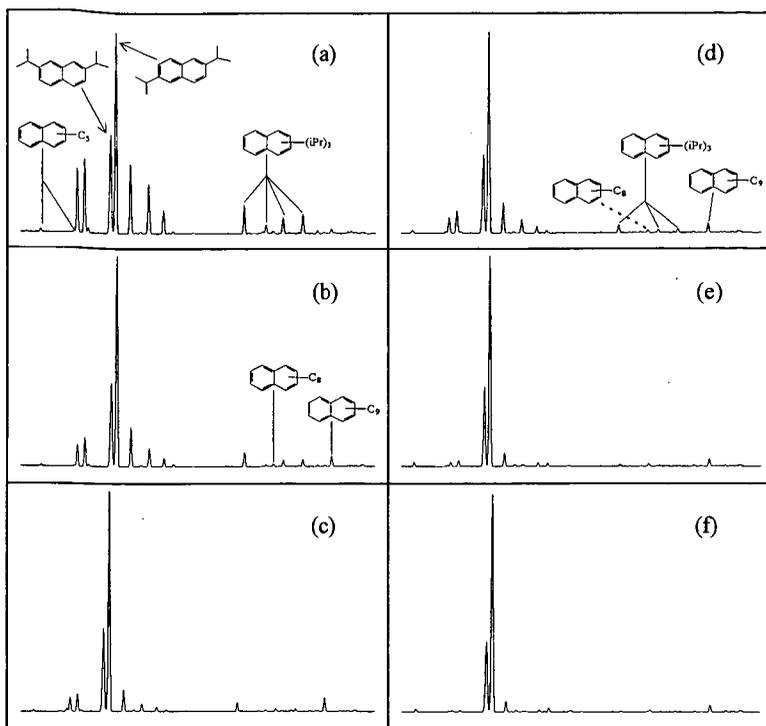


Figure 1. Comparison of the polyalkylated naphthalene region of the gas chromatograms for 2 h catalytic runs at 200 °C, 1 g naphthalene, and propylene/naphthalene = 0.5. Parts (a) through (c) are neat runs with 0.10 g catalyst charge: (a) HM14, (b) HM71, and (c) HM230. Parts (d) through (f) compare 0.15 g HM74 charge with (d) no added water, (e) 40 mg added water, and (f) 120 mg added water.

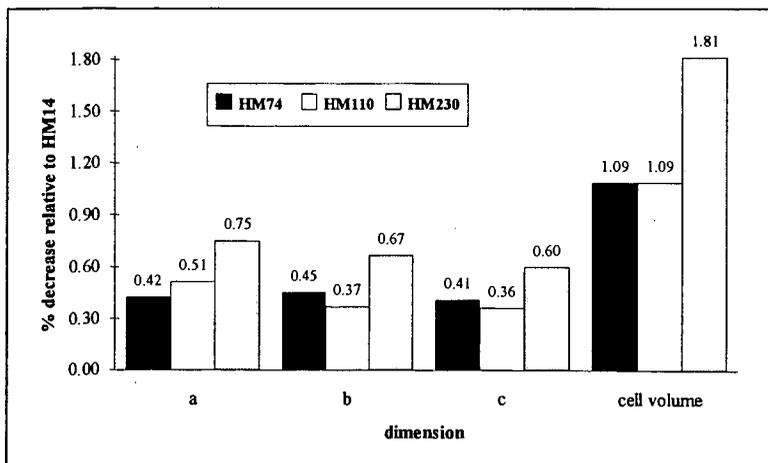


Figure 2. Percentage decreases in cell constants and cell volumes as a result of dealumination. Calculations relative to the cell dimensions determined for HM74.