Conversion of Propylene and Butylene over ZSM-5 Catalyst

Using the zeolite ZSM-5, new technology has been developed for catalytically oligomerizing light olefins (C_3 to C_4) to gasoline (C_5 to C_{10}) and diesel (C_{10} to C_{20}) range product. This reaction produces product constrained by both the shape selectivity of the zeolite catalyst and the thermodynamics governing the oligomerization reaction.

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SCOPE

Many refinery and synthetic fuel processes produce large amounts of light C_3/C_4 olefins which can then be catalytically oligomerized to gasoline- or diesel-range products. A new development in this area is the use of shape-selective zeolite catalysts. This reaction has been studied over ZSM-5 catalyst to determine what effect shape selectivity has on product chemistry and to determine what effects thermodynamics have on constraining molecular weight. The relationship of these effects to commercial oligomerization technology is also discussed.

CONCLUSIONS AND SIGNIFICANCE

The reaction of light olefins over ZSM-5 catalyst was found to proceed sequentially by reaction to discrete oligomers, followed by cracking and copolymerization. The shape of the product molecules is governed primarily by the pore structure of zeolite catalyst. The product molecular weight is shown up to ~625 K to be governed by the kinetics of the reaction, dependent on temperature, pressure, and space *velocity. Above* ~625 K equilibrium constraints become important and limit the molecular weight of the product.

Experimental

In *general, all* experiments were conducted in high-pressure pilot-plant reactors capable of operating up to approximately 18,000 kPa. The reactors used were enclosed in either a three- or four-zone furnace with an isothermal zone, holding from 10 to 100 cm^3 of catalyst. Reactor pressure was maintained by a gas phase backpressure control valve, while liquid depressurization was by liquid level control on a high-pressure phase separator. Product analysis was by both gas chromatography and mass spectrometry.

Introduction

It has long been known that acid-type catalysts will oligomerize light olefins to higher molecular weight products (Oblad et al., 1958). In 1935 this chemistry was commercialized to produce gasoline-range iso-olefins (C_6–C_{10}) from propylene (C_3) and butylene (C_4), using phosphoric acid impregnated on silica clay (Ipatieff and Egloff, 1934).

Over the past several decades Mobil Research and Development Corporation has been active in developing process technology based on olefin reactions over zeolite catalysts (Meisel and

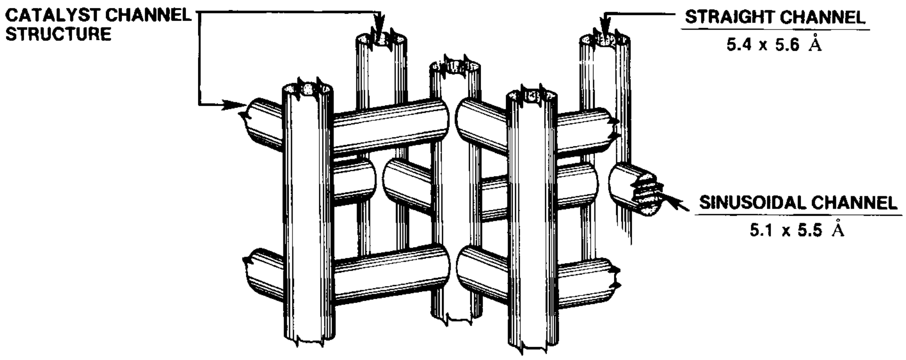

Figure 1. ZSM-5 Catalyst.

Weisz, 1982). The majority of this effort has used the Mobil synthetic zeolite, ZSM-5. This has resulted in a new process, MOGD (Mobile olefin to gasoline and distillate) (Tabak, 1984), which uses the ZSM-5 class of zeolites to convert light olefins to higher molecular weight gasoline and diesel fuel (Tabak, 1984; Garwood, 1982, 1983).

This paper discusses the phenomena of shape-selective olefin reaction over ZSM-5 in three sections:

- Catalyst and Chemistry
- Thermodynamic Constraints
- Commercial Process

Catalyst and Chemistry

This process chemistry is based on a unique synthetic crystalline material ZSM-5 (Kokotailo et al., 1978; Argauer and Landolt, 1972). Depicted schematically in Figure 1, the catalyst is characterized by a series of channels that run in two directions and are about 5.5 Å (0.55 nm) in diameter. While it is protonic acid sites within the catalyst that perform the reaction, it is the shape and diameter of the pores that control the shape and size of the product molecules. This "product selectivity" characteristic of ZSM-5 is well known, and other reaction products, such as those from the methanol to gasoline reaction (Meisel and Weisz, 1982) and the alkylation of toluene with methanol (Chen et al., 1979), exhibit this selectivity. In the MOGD process, this product selectivity results in an iso-olefinic product with a well-defined structure.

Figure 2 shows a model reaction path for propylene. As shown, there are four distinct reactions occurring. First, propylene will oligomerize to distinct C_6, C_9, C_{12}, etc., oligomers. These then isomerize and recrack, forming a range of light olefins. Lastly, these then repolymerize to an equilibrium (or pseudo-equilibrium) distribution of heavier iso-olefin. As a result of having both forward (polymerization) and reverse (cracking) reactions, a continuous carbon number distribution occurs in the product which can be independent of the carbon number of the starting olefin. For example, Garwood (1982, 1983) has previously shown, at constant temperature and pressure, identical product distribution for feedstocks of ethylene (C_2=), propyl-

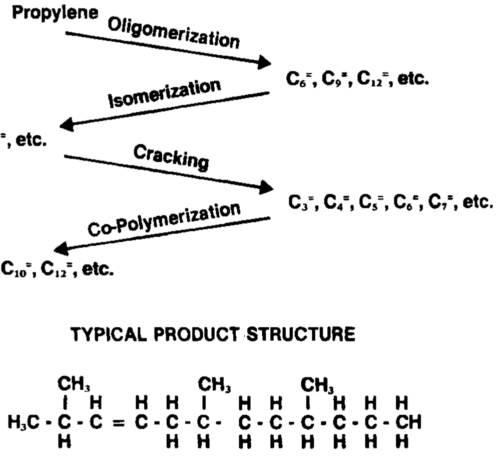

Figure 2. Model reaction path for propylene.

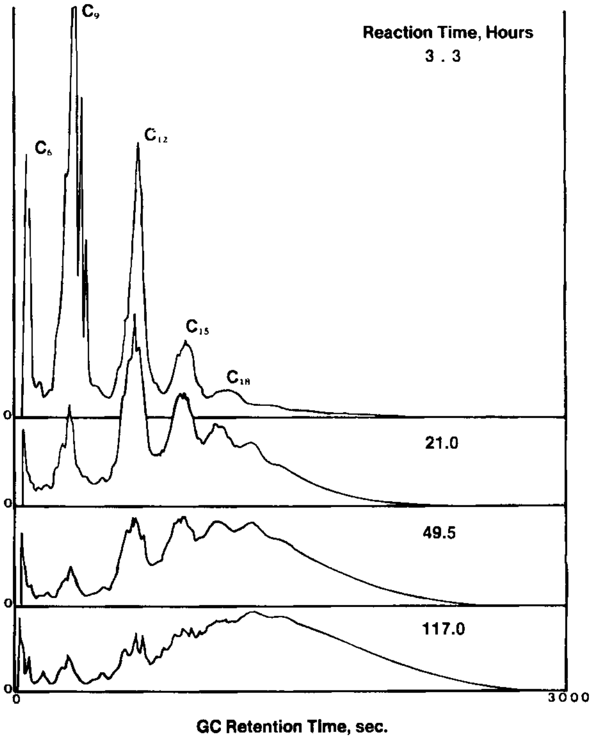

Figure 3. MOGD product distribution during oligomerization at 448 K.

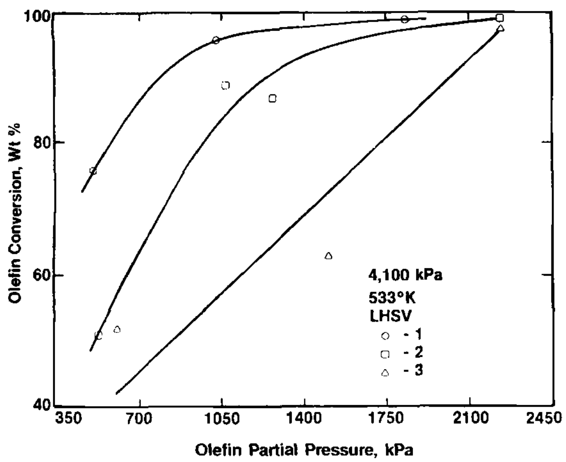

Figure 4. MOGD of synthetic C_3/C_4 mix at various olefin partial pressures.

ene ($C_3{=}$), pentene ($C_5{=}$), hexene ($C_6{=}$), and decene ($C_{10}{=}$).

This sequential reaction can be seen in Figure 3, which shows the gas chromatogram of product sampled from a batch autoclave experiment processing propylene ($C_3{=}$) with ZSM-5. For short contact times, primarily oligomers are produced. This is shown by the sharpness of the peaks at the retention times for C_6, C_9, C_{12}, etc., at 3.3 h reaction time. At longer contact times (21 and 50 h) this peak sharpness disappears as more intermediate carbon numbers are produced by copolymerization. Eventually an almost continuous carbon number distribution is shown, with little predisposition to oligomers.

Structurally the final product is influenced by the pore structure of the catalyst. For low carbon number products (i.e., C_4, C_5) the isomer distribution is approximately at equilibrium (Garwood, 1982, 1983). For the higher carbon numbers, the structure is primarily methyl-branched olefinic chains, Figure 2, with the maximum cross section of the chain limited by the 5.4 × 5.6 Å dimension of the largest ZSM-5 pore. At conditions chosen to maximize diesel fuel-range products (C_{11}–C_{20}), analysis has shown the product to be essentially 100% olefinic with ~10% or less of the double bond in the alpha position. Overall branching is not extensive, with most branches being methyl at about one branch per five carbon atoms.

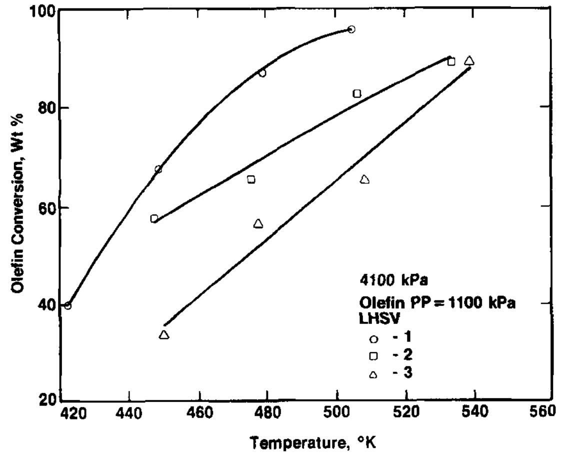

Figure 5. MOGD of synthetic C_3/C_4 mix at various temperatures.

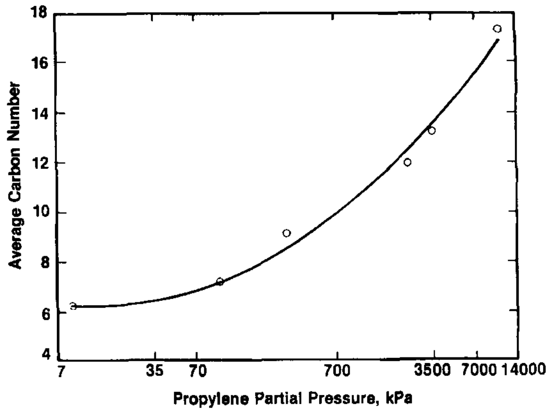

Figure 6. Effect of olefin pressure on product.

While catalyst pore size determines product structure, the conditions of the reaction (temperature, pressure, and space velocity) determine product molecular weight. Overall, the reaction window for olefins over ZSM-5 is large, with reactions having been demonstrated for temperatures as low as 310 K (Tabak, 1981) and pressures as low as 7 kPa (Garwood, 1982, 1983), and as high as 14,000 kPa. In general, there will be no upper limit to reaction temperature. However, as will be shown, equilibrium constraints become significant at about 600 K.

All three variables—temperature, pressure, and space velocity—are interactive. This is shown in Figures 4 and 5 for a synthetic blend of propylene/propane/1-butene/isobutane (17/10.7/36.1/27.2 wt. %). Olefin partial pressure was varied by nitrogen purge. As expected for initial C_3/C_4 olefin conversion, high conversion is favored by high temperature, high pressure, and low space velocity. The initial C_3/C_4 conversion is second-order.

Commercial interest in this reaction is at conditions where there is essentially complete conversion, and the primary effect of the process variables is to alter average product molecular weight. Figures 6 and 7 show the effect of temperature and pressure for conditions of essentially complete olefin conversion. The effect of pressure is straightforward; thermodynamically high pressure always favors high molecular weight, and this effect is

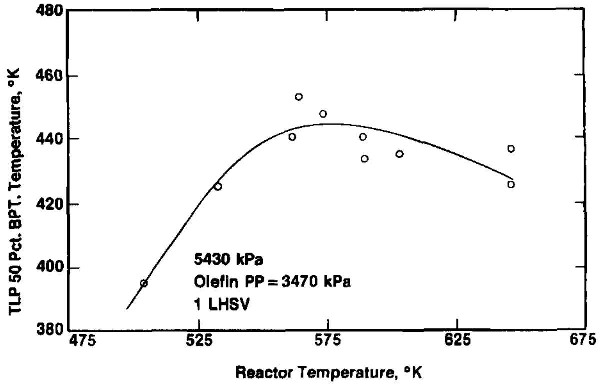

Figure 7. Effect of reactor temperature on 50% point.

Table 1. Comparison of Calculated and Observed Olefin Equilibria*

Charge Pressure (kPa) Products wt. %	(T = 550°K) Charge Pressure $C_3{=}$ 5.5 kPa Data**	Calc.	$C_5{=}$ 9.0 kPa Data*	Calc.	$C_6{=}$ 10.3 kPa Data*	Calc.
$C_2{=}$	<0.1	0.7	<0.1	0.5	<0.1	0.4
$C_3{=}$	8	5.3	10	4.1	9	3.8
$C_4{=}$	28	23.9	20	20.2	20	19.1
$C_5{=}$	30	21.2	27	19.6	23	19.1
$C_6{=}$	13	23.2	15	23.6	16	23.6
$C_7{=}$	11	12.5	11	13.9	10	14.3
$C_8{=}$	6	6.5	7	8.0	8	8.4
$C_9{=}$	3	3.4	5	4.5	6	4.9
$C_{10}+$	1	3.5	5	5.6	8	6.4

*T = 550 K
**Data of Garwood (1982, 1983)

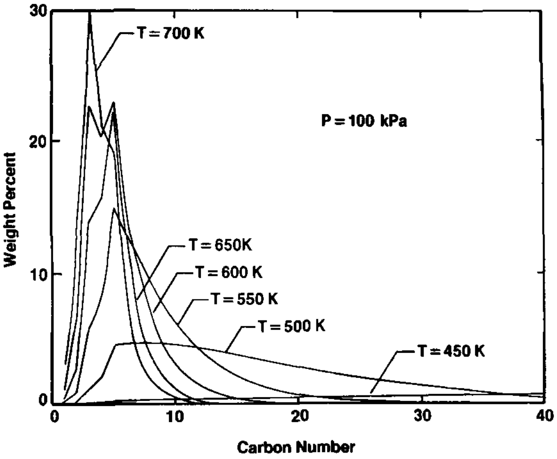

Figure 8. Effect of temperature on olefin equilibrium.

seen in Figure 6. For temperature, Figure 7, two effects can be observed. Initially, increasing temperature will increase product molecular weight. For this region, as temperature increases the rate of polymerization increases, and the product molecular weight therefore increases. However, at a certain point the cracking reaction will dominate. Thus, increasing temperature in this region will lower product average molecular weight. This maximum with temperature shows the interaction of the two dominant reactions, cracking and polymerization, and how they can control product molecular weight.

Equilibrium Considerations

As indicated in the previous section, the conditions that can be used for condensation of light olefins overlap those for cracking of large paraffins or olefins. Thus consideration of chemical equilibrium can clarify the effects of process conditions on yields of heavy hydrocarbons obtainable. The problem in calculating equilibrium yields is that extremely large numbers of compounds are involved and very few of the required free energy data are available. For example the number of olefin isomers with 25 carbon atoms is about 12.7 billion (Read, 1976). Since the size of product molecules can extend to 40 carbon atoms and more, the equilibrium state involves an astronomical number of individual compounds.

The computations can be greatly simplified by the fact that when a group of isomers are in equilibrium with each other they can be treated as a single compound in calculating their equilibrium with other compounds. Calculating the lumped free energy of the isomer group exactly still requires knowledge of the individual isomer free energies, however, and these are currently known only up to six carbon atoms.

Alberty (1983) has developed an approximate technique for the olefins by calculating the isomer group thermodynamic properties from the known values for compounds up to six carbon atoms and extrapolating to higher carbon numbers using a constant increment per carbon. These should give reasonable estimates if they are not extrapolated too far. They include, however, many isomers that are excluded from the pores of ZSM-5 catalyst by steric hindrance. Thus for our system we need to estimate properties of groups containing only those isomers for which the catalytically active pores of the zeolite are accessible. Another consideration is the departure of the system from ideal gas behavior. Under the conditions used for high yields of distillate fuels the system approaches supercritical dense-phase conditions. Thus the best approach seems to be to

Table 2. Thermodynamic Data Used in Equilibrium Calculations*

	(T = 600°K) ΔH_f^0	ΔG_f^0
$C_2{=}$	10.60	20.92
$C_3{=}$	1.98	26.46
$C_4{=}$	−6.99	32.59
$C_5{=}$	−13.71	40.38
$C_6{=}$	−20.24	47.85
A	19.49	−1.95**
B	−6.63	8.30**

*T = 600 K
**Modified from original values of 2.13 and 7.36, respectively.
ΔH_f^0 – standard enthalpy of formation
ΔG_f^0 = standard Gibbs free energy of formation

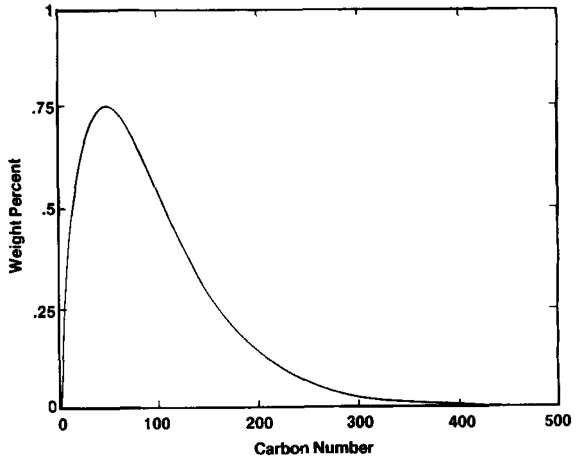

Figure 9. Olefin equilibrium at 450 K and 100 kPa.

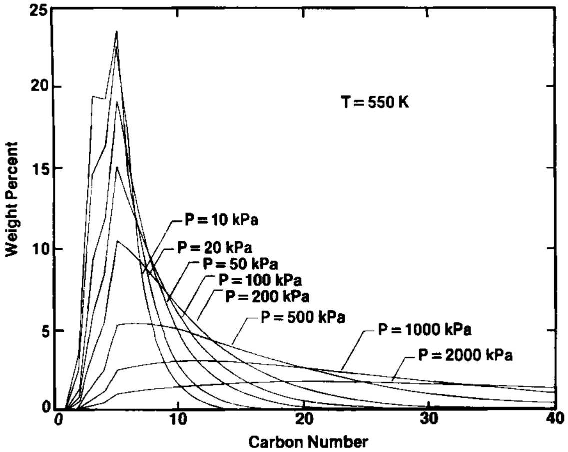

Figure 10. Effect of pressure on olefin equilibrium.

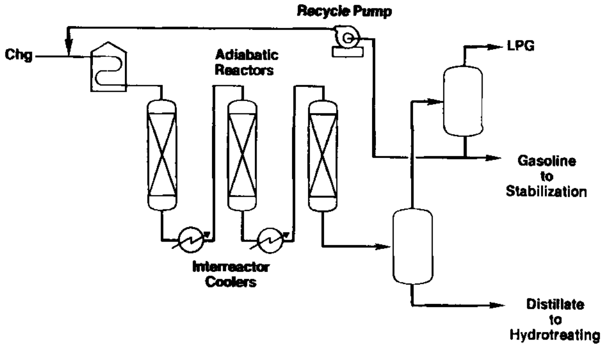

Figure 12. MOGD process flow, maximum distillate mode.

develop free energy values that include fugacity coefficients by fitting experimental equilibrium data obtained with ZSM-5 catalyst.

Data on olefin equilibration over ZSM-5 have been reported previously (Garwood, 1982, 1983). When these are compared with equilibrium calculations using Alberty's extrapolated free energy data, it is found that the higher carbon numbers are overpredicted, possibly because not all the isomers that theoretically exist can be accommodated by the ZSM-5 framework. It was found, however, that reasonable predictions could be made by adjusting the slope used in extrapolating the free energies. Some of these predictions, using a computer program for equilibrium calculations (Krambeck, 1978), are compared with typical data from Garwood in Table 1. In this calculation Alberty's heat of formation data were used without modification to adjust for temperature. The values used are given in Table 2, where *A* and *B* are the intercept and slope used in the linear extrapolations of enthalpy and free energy (e.g., $\Delta G_f^0 = A + Bn$, where n is carbon number).

Using these same values we have estimated the effect of temperature on equilibrium yields in Figure 8. These results, which are for an olefin pressure of 100 kPa, show that at temperatures of 550 K and above the equilibrium product is predominantly gasoline (C_{10} and lighter) rather than distillate (C_{11}–C_{20}). As temperature is reduced, the product can be much heavier, as illustrated in Figure 9 for a temperature of 450 K. Of course with such high molecular weight products the assumption of ideal gas behavior is obviously wrong and estimates of fugacity coefficients should be included in the calculation. However, the basic conclusion, that at these conditions equilibrium does not limit conversion to distillate, would be unaffected.

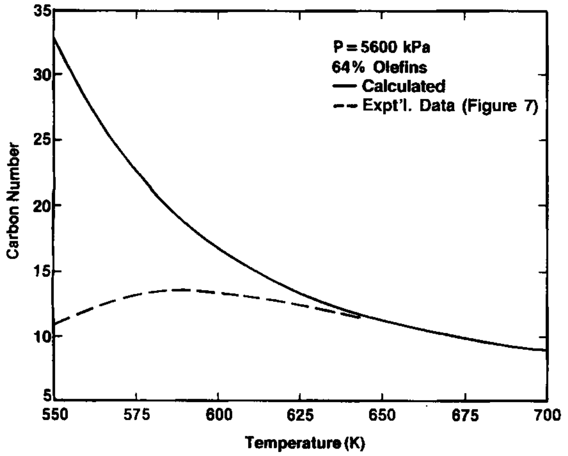

Figure 11. Average carbon number at equilibrium.

Similar calculations on the effect of pressure are shown in Figure 10 for a temperature of 550 K. These show how increasing olefin pressure can allow more distillate production. Again, caution must be used in interpreting the higher molecular weight results, as condensed phases will form.

Calculations under the conditions of Figure 7 are shown in Figure 11. In spite of the approximations involved, they are consistent with the observed decline in average carbon number at higher temperatures, and are in reasonable agreement at about 625 K.

Commercial Process

In translating these olefin reactions to a large-scale process, several practical concerns must be met. The two major concerns for MOGD were controlling the heat of reaction and maximizing the yield of either gasoline- or distillate-range products. To control the heat of reaction (~1,550 kJ/kg of propylene when

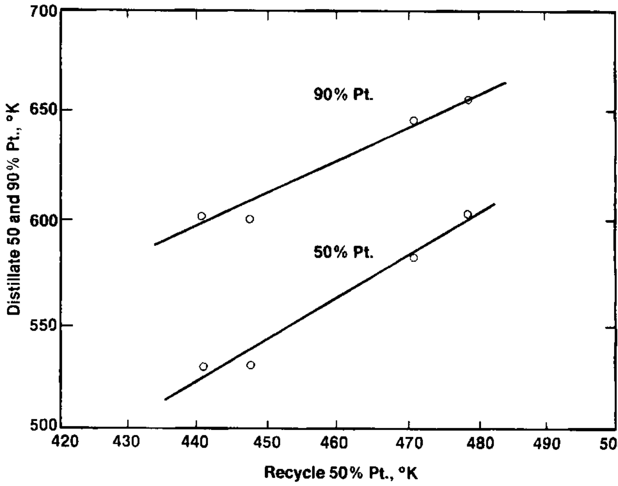

Figure 13. Effect of recycle cut point.

Table 3. MOGD Product Quality

	Distillate	
	Raw	Hydrotreated
Specific gravity 15°/15°	0.79	0.78
Bromine no.	79	4.0
Aromatic, vol. %	—	3.0
Pour point, °C	<−50	<−50
Viscosity, cs @ 40°C	—	2.5
Cetane no. (Engine)	33	56
Sulfur, wt. %	<0.002	<0.002
90% B.P., °C	333	343
	Gasoline	
Specific gravity 15°/15°	0.73	
Octane	92	
R + O	92	
M + O	79	

making diesel-range product), a combination of interreactor cooling and liquid recycle was used. Figure 12 shows a conceptual MOGD plant using three reactors with interstage cooling and a condensed liquid recycle (Capsuto et al., 1983; Owen et al., 1984).

While liquid recycle provides a heat sink for control of the reaction exotherm, it also affects product quality by allowing material to be recycled, and thus re-reacted. In our MOGD conceptual design, both maximum gasoline and maximum diesel modes can be run by shifting of reactor temperatures and recycle composition (Tabak, 1984). The effect of recycle is shown in Figure 13 where average product molecular weight shifts with average recycle molecular weight; the effect being that as recycle gets heavier, product gets heavier.

As discussed earlier, this work grew out of development of this chemistry to produce gasoline and diesel from light olefins. Table 3 shows product properties of the gasoline-range and diesel-range material. As shown, the light (C_5–C_{10}) product makes excellent gasoline, and the heavier product (C_{11}–C_{20}), after hydrogenation, makes excellent diesel fuel. Of particular note are the high octane of the iso-olefinic gasoline, and the high cetane number and low pour point of the iso-paraffinic diesel.

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