



CHALLENGES FOR HYDROCRACKING DMO/VGO FEEDSTOCK

Jamal A. Anabtawi¹

1: ES Technology, Saudi Aramco, Box 8970
Dhahran 31311, Saudi Arabia

E-mail: jamal.anabtawi@aramco.com

ABSTRACT

Hydrocracking of demetallized oil is a unique problem, due to its high carbon content and low priority for catalyst manufacturers to develop a suitable catalyst system. Pilot plant testing of commercial catalysts is a complex task due to difficulty of process simulation, scale of operation, and the fact that the hydrotreating/hydrocracking combined performance is considered. This will not allow detail knowledge about each of the composite catalyst system. Hydrocracking catalyst performance is controlled by their structure and composition, in particular acidity, metal/acid balance, pore distribution, metal type and concentration, surface area and crystallite size of the zeolite. The importance of each property determines the hydrogenation and cracking activity, and catalyst life. In an effort to search for suitable catalyst system for hydrocracking demetallized oil (DMO) / vacuum gas oil (VGO), pilot plant studies are often carried out to provide technical independent information on commercial catalysts. The performance of two (hydrotreating/hydrocracking) catalysts systems was evaluated in a pilot plant under commercial operating conditions for DMO/VGO blend. The catalysts activity (SOR) temperature, selectivity to middle distillate, and quality of product fractions were compared. The pilot plant tests were conducted at a 75% conversion of 375°C⁺ fraction in a once-through hydrogen mode; other conditions were similar to the commercial hydrocracker. The C₅⁺ liquid products were fractionated into light and heavy naphtha, kerosene, light and heavy diesel cuts and fractions characterized. The catalysts were characterized before and after pilot plant tests for their physical, chemical, and surface properties. This paper presents the pilot plant and catalyst characterization data and proposes research areas for catalyst improvement.

Keywords: Catalysts performance Hydrocracking Vacuum gas oil Demetallized oil Pilot plant

INTRODUCTION

Hydrocracking has a key function in a refinery producing transportation fuels from heavier fraction. Recent challenge for the hydrocracking process is to develop a catalyst system that can meet the market needs, profitability, product yields and strict fuel quality specifications. Process developments include single vs. two stages, once through vs. recycle mode, a common vs. separate recycle stream, single reactor containing different catalysts vs several reactors containing individual catalysts [Minderhound, 1999]

In view of strong pressures to increase refinery margins, great interest has been shown to optimizing and revamping existing hydrocrackers. In order to achieve this goal the following options need to be considered:

- Use improved and tailor-made catalysts;
- Process heavier and /or cheaper feedstock;
- Produce more valuable products by shifting the product slate (selectivity)
- Increase throughput and thus equipment utilization

Increase cycle length through proper maintenance, improved reliability, and process control/optimization model [Minderhound, 1993].

Hydrocracking catalysts are bi-functional in nature: consisting of an acidic function leading to cracking, and metal function responsible for hydrogenation and dehydrogenation reactions. The optimum function of a catalyst is to balance these two functions in relation to the feedstock quality and fuels desired [George, 1994]. Catalyst design is crucial for effectively hydrocracking heavy feedstocks at high cracking activity, middle distillate selectivity, and

product quality. A typical hydrocracking catalyst system consists of two catalysts used in series: the first stage pretreatment catalyst is essential to remove hetero-atoms (metals, N, S); the second stage catalyst, a zeolitic-based and sensitive to nitrogen, can produce higher conversion. A suitable catalyst combination is able to maintain conversion, product selectivity and quality without causing excessive coke lay-down. This can be achieved by optimizing the catalyst acidity, hydrogenation activity, the acidity-hydrogenation balance and porosity profile [Antos, 1999].

DMO processing poses unique problems to hydrocracking catalyst systems in limiting the performance of available commercial catalysts. Due to limited demand for catalysts used in this application, catalyst manufacturers are not investing in the development of improved catalyst systems. This is evident from the few available catalyst systems for this application. In this study, two catalysts were tested in a pilot plant under commercial conditions to determine their suitability for DMO service. The performance was based on activity Start-of-Run (SOR) temperature, selectivity to diesel, and product quality.

EXPERIMENTAL PROCEDURES

Catalyst Characterization

Fresh catalysts were analyzed as received. Spent catalysts from pilot plant studies were first washed with solvent to remove residual oil trapped in catalyst pores. The solvent washed samples were then dried at 130°C and crushed to a fine powder prior to characterization for surface area, pore volume, elemental analysis and loss on ignition (LOI).

Feed Analyses

The feedstock used in this study was a blend of 18.9 vol. percentage Demetallized Oil (DMO) in VGO. The quality of prepared batches, used in the pilot plant tests, was checked for consistency by GC simulated distillation and density analyses. The feedstock components were characterized using standard procedures given in Table 1. These results show that the DMO, although demetallized was high in sulfur, nitrogen, and carbon residue. The DMO/VGO blend contained 2.66 wt. percentage sulfur, 1290-PPM nitrogen and 91.5 vol. percentage 375°C⁺ residue.

Pilot Plant procedures

Performance testing of candidate catalyst systems (A and B) was carried out in a pilot plant, details of which was given elsewhere [Anabtawi, 1998]

Catalyst Loading

A two-staged catalyst system, consisting of hydrotreating catalyst first stage (2/3) and hydrocracking catalyst (1/3), was loaded in a trickle bed down-flow reactor. The total catalyst volume was diluted with inert (silicon carbide, 3.4 mm) in 1:1 volume ratio. Silicon carbide layers (38 mm) were also inserted as the post heat (bottom) and pre-heat (top) layers and to separate the two catalyst zones.

Catalyst Pretreatment and Start-up Procedures

The catalyst was then dried in situ at 140°C, 570 psig and helium flow for 16 hours. The catalyst systems were sulfided by using a dimethyldisulfide-straight run kerosene (as per manufacturer's procedures) to insure conversion of the catalyst from the oxide to the sulfide form. In addition to the presulfiding procedure, straight run kerosene (0.08 wt. % sulfur content) was then further used to both pre-wet and further sulfide the catalysts. The DMO/VGO feed was then introduced at 300°C and the temperature was raised to 345°C at 15°C/h. Upon reaching 345°C, the temperature ramp to 385°C was carried out at a slower rate of 10°C/h. The run was initiated at 385°C whilst maintaining all operating parameters at design conditions shown in Table 2.

Table 1. VGO, DMO and Feed Stock Blend Analyses

Analyses	ASTM Method	VGO	DMO	Blend
Density, g/cc	D-4052	0.9233	0.9735	0.9312
Heptane-Insoluble, wt. %	IP 143/78	<0.01	0.015	0.097
MCR, wt	D-4530	0.53	9.44	2.40
Sulfur, wt. %	D-5453	2.62	3.36	2.66
Nitrogen, wt. %	D-4629	652	1620	1290
Nickel, PPM	ICP	N<1	3	< 1
Vanadium, PPM	ICP	N<1	11	2.0
TBP Residue 375°C ⁺ , vol. %	D-2892	ND	ND	91.5
Simulated Distillation, vol. %	D-2887			
IBP-85 °C		0.0	0.1	0.0
85-1855 °C		0.1	1.2	0.1
185-240 °C		0.3	4.3	0.5
240-315 °C		1.9	12.4	2.0
315-375 °C		7.5	4.2	5.5
375-FBP °C		89.2	76.9	91.8

ND: Not determined

Table 2. Pilot Plant Operating Conditions

Reactor Pressure, psig.	2135
Target ΔT between Pretreat and Hydrocracking catalysts beds, °C	0
Target Conversion of 375°C ⁺ , wt. %	75
Liquid Hourly Space Velocity (LHSV), h ⁻¹	0.440 (a)
Liquid Hourly Space Velocity (LHSV), h ⁻¹	0.624 (b)
Hydrogen to Hydrocarbon Ratio, NL/L	1200

(a) Based on total catalyst volume (b) based on hydrotreating catalyst

RESULTS AND DISCUSSION

Two pilot plant runs were carried out in a once-through gas and liquid mode, a DMO/VGO blend under conditions similar to the commercial hydrocracking unit. The response of catalyst activity to a change in process parameter was slow, thus the change in product quality was somewhat sluggish. To minimize this effect, the product was sampled on a 24-h basis, while the product selectivity was based on a product sample collected over a 5-day period. Each pilot plant run was started at 385°C and then raised to achieve the 75% 375°C+ conversion. The Weight Average Bed Temperature (WABT) was calculated using the following:

$$\text{WABT} = 2/3 \text{ HT temp.} + 1/3 \text{ HC temp.}$$

The catalyst activity defined by the SOR temperature to attain the target conversion, and product quality and C₅⁺ liquid yield structure was used to determine the catalyst selectivity.

Catalyst Characterization

The physical properties were determined for the two catalyst systems including: BET surface area, pore volume, and average pore radius, metals and poisons, and Loss on ignition. Table 3 compares the physical properties (before and after pilot plant tests), while Table 4 gives the metal analysis of both catalyst systems. In general, the loss in the surface area and pore volume and increase in pore diameter was the result of carbon lay-down on the catalyst. Moreover, vanadium, and iron deposited mainly on the hydrotreating catalysts.

Catalyst System A

Results (Table 4) showed that the HT catalyst (A) contains 9.6 wt.% W and 0.93% Ni supported on alumina. The equilibrium sulfur on the spent catalyst samples was about 2.2 wt. percentage, and carbon deposition of 7 wt. percentages. Trace analysis of the catalysts after used showed significant deposition of vanadium and iron and traces of calcium and sodium.

Table 3. BET Surface Areas and Pore Volume of HT and HC Catalysts (A & B)

Description	Carbon Wt.%	Surface Area m ² /g	Surface Area Loss, %	Pore Volume cc/g	Loss Pore volume, %	Pore Diameter Å	PD Loss %
Catalyst System A							
Fresh HT	T	265		0.54		82	
Used HT	7.0	212	5.5	0.39	27	73	11
Fresh HC	T	429		0.39		36	
Used HC	11.3	62	85.5	0.15	38	94	161
Catalyst System B							
Fresh HT	0.1	164		0.40		105	
Used HT	6.2	150	8.5	0.13	68	114	8.6
Fresh HC	.1	258		0.35		72	
Used HC	5.4	213	17.4	0.22	37	94	30.6

Table 4. Bulk and Trace Elemental Analysis

Catalyst Description	LOIa Wt. %	Mo Wt.%	Ni Wt.%	W Wt.%	P Wt.%	V PPM	Fe PPM	Ca PPM	Na PPM	Al Wt.%	C Wt.%	S Wt.%
Fresh HT	4.5	-	0.93	9.6	NP	T	T	T	0.1	11.0	T	0.1
Used HT	14.3	-	1.0	8.8	NP	1173	204	104	T	10.8	7.0	2.2
Fresh HC	6.4	-	0.51	5.4	NP	T	T	T	0.1	17	T	0.1
Used HC	17.9	-	0.6	5.1	NP	75	568	72	175	16.7	11.3	1.2
Fresh HT	1.2	12.5(13)	3.2 (3)	NP	2.8	146	167	156	384	36.6	0.1	0.3
Used HT		11.5	2.7	NP	2.2	436	203	130	363	33.4	6.2	5.9
Fresh HC	2.1	NP	4.4	16.8	NP	41	59	171	217	31.2	0.1	0.2
Used HC		NP	3.5	17.1	NP	27	128	199	167	27.4	5.4	4.8

- Loss on Ignition at 550°C () manufacturer specifications

The HC catalyst contains an active metal content of 5.4 wt. percentage W and 0.5 % Ni supported on silica-alumina. The equilibrium sulfur on the spent catalyst samples was about 1.2 wt. percentage, and carbon deposition was ~11 wt. percentage, which is somewhat higher than the first stage hydrotreating catalyst. Trace analysis of the used catalysts showed insignificant metal deposition compared to the deposition on the hydrotreating catalyst. These results indicated that the hydrocracking catalyst faced higher coke lay-down compared to the

hydrotreating catalyst, thus the surface area and pore volume dropped by 85.5% and 62% respectively, after use. The average pore radius, which is slightly larger after use, indicating that coking had either selectively plugged smaller pores or that pore damage had caused this increase in pore radius.

Catalyst System B

The observed major metal concentrations in the fresh HT catalyst were 3.2 wt. percentages Ni, 12.5 wt. percentages Mo and 2.8 wt. percentage phosphorous used as a promoter. Similarly the observed for the HC catalyst bulk concentrations of Ni and W were 4.1 wt. percentage and 16.8 wt. percentage respectively. The trace metal concentrations, mainly vanadium was observed on the used hydrotreating catalyst and was negligible on the hydrocracking catalyst. The levels of other trace metal levels on all the catalyst samples are below detection limits.

The hydrocracking catalyst faced higher deactivation compared to the hydrotreating catalyst, thus the surface area and pore volume dropped by 17% after use (compared with 8.5% for the HT catalyst). However, the pore volume decrease in HT catalyst was more significant. The average pore radius, which is slightly higher in the after use, indicating that coking had either selectively plugged smaller pores or that pore damage had caused this increase in pore radius.

Catalyst Performance

Catalyst Activity

The catalyst activity data was plotted as conversion and WABT vs. time on stream as shown in Figures 1 and 4 for catalyst systems A and B, respectively. Figure 1 shows that the steady state conversion for Catalyst A was 77.8% achieved at a WABT of 385°C. The activity was stable for the steady state 170-240 hour period. Figure 2 shows that Catalyst B gave ~45% conversion at 385°C, and temperature had to be raised to 405°C in order to achieve the target conversion about 75%. The steady state product used to evaluate selectivity and product quality, was collected over the period 190-310 h. This study showed that the target conversion was achieved at SOR temperature of 385°C for Catalyst A and 405°C for Catalyst B. This higher SOR temperature will result faster deactivation rate, thus reducing the catalyst operating cycle length.

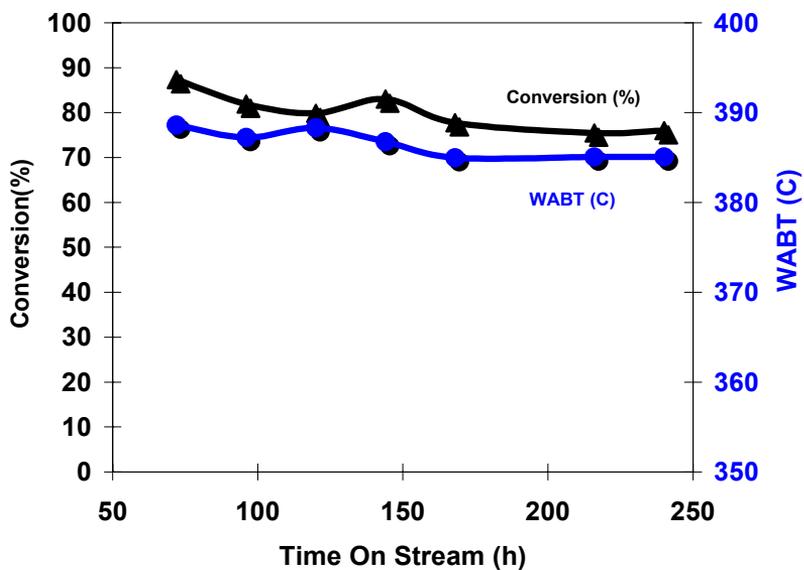


Figure 1. Activity as a Function of Time on Stream for Catalyst System A

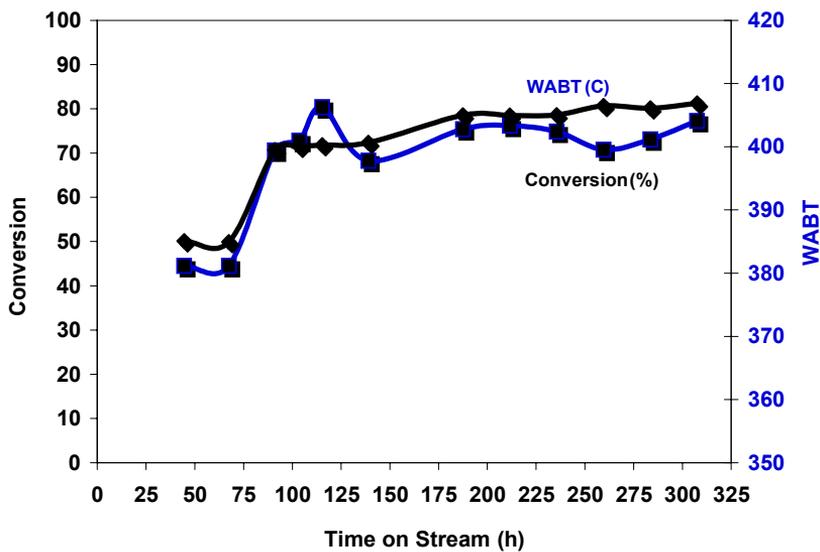


Figure 2. Activity as a Function of Time on Stream for Catalyst System B.

Catalyst Selectivity

The performance of catalyst systems was also evaluated based on their product distribution. An ideal catalyst minimizes gas and coke production and maximizes liquid product yield and quality. In addition, selectivity to middle distillate is a prime consideration for the catalyst selection. Figures 3 and 4 show the conversion and naphtha, kerosene and diesel selectivity as a function of time on stream for the two catalyst systems, respectively. Catalyst A, containing Ni-W in both hydrotreating and hydrocracking catalysts, gave 49%, 14%, and 22% naphtha, kerosene, and diesel selectivities, respectively. In spite of the lower temperature used, the catalyst produced more cracking activity leading to higher selectivity to lighter fractions. This could be due to the higher zeolitic content and acidity of the catalyst. On the other hand, Catalyst B gave 32%, 15%, and 28% naphtha, kerosene and diesel selectivities, although it was operated at 20°C higher temperature. This could be due to the lower hydrogenating activity of the Ni-Mo first stage catalyst causing the hydrocracking catalyst not to function. It is expected that at such higher WABT cracking will increase, if the hydrocracking catalyst is well designed. Research work is needed to evaluate each hydrotreating and hydrocracking catalysts separately to identify important design factors for an optimum catalyst system.

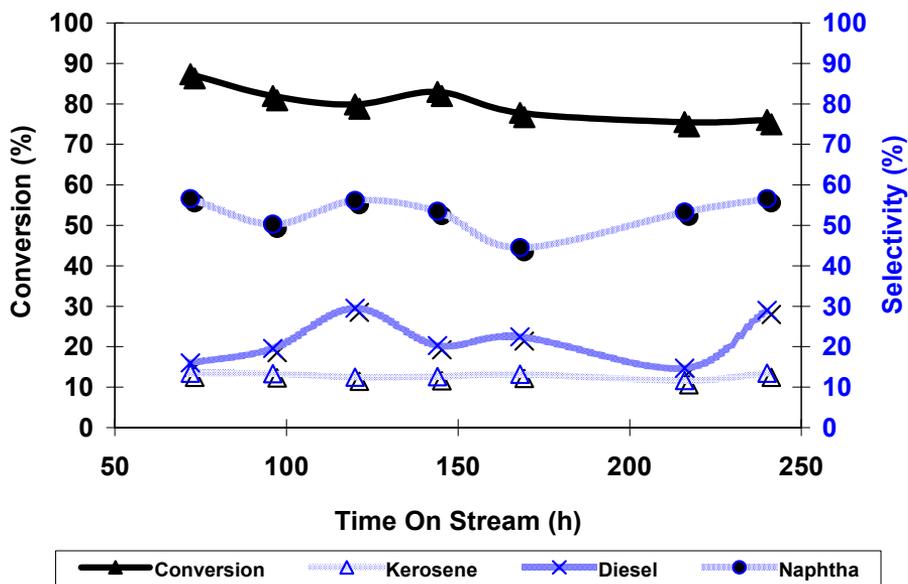


Figure 3. Selectivity as a Function of Time on Stream for Catalyst System A.

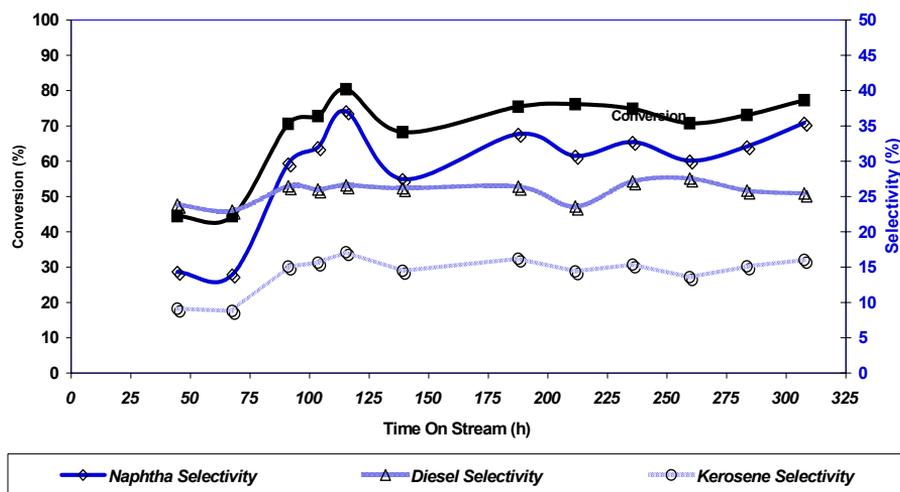


Figure 4. Selectivity as a Function of Time on Stream for Catalyst System B.

Product Quality

The product quality for each pilot plant run was based on a composite sample, which incorporated all the product samples collected during steady state operation. The C_5^+ composite liquid samples from each pilot plant test were fractionated using true boiling point distillation (ASTM Method D-2892) into the following fractions:

Product Fraction	Boiling Range
Light Naphtha	C5-85°C
Heavy Naphtha	85-185°C
Kerosene	185-240°C
Light Diesel	240-315°C
Heavy Diesel	315-375°C
Distillate	185-375°C
Residue	375+°C

The distilled fractions were further analyzed for specific properties to determine the performance of the two catalyst systems. Table 5 shows the results of detailed analyses light and heavy naphtha, kerosene, light and heavy diesel and residue. In general, Catalyst A products showed higher sulfur, density, and in general less hydrogenation. This is due to the

lower temperature, therefore, less severity for hydrogenation; however, the differences in product qualities were insignificant.

The refinery hydrocracking catalyst objective is to produce middle distillates with excellent product qualities. Jet and diesel fractions can be obtained with very low sulfur contents (<20ppm), and very good combustion properties (kerosene smoke point >25 and diesel cetane number >55). Both catalyst systems could not achieve these specifications. The optimum catalyst system should be able to remove heteroatoms, and produce deep aromatic saturation. For an efficient system both catalysts have a well balanced bi-functional properties (hydrogenation and acidic functions for good activity and stability. Catalyst A is a better option, due to its higher activity leading to longer life cycle, but has lower diesel selectivity.

CONCLUSIONS

Two pilot plant tests were conducted to evaluate the performance of two catalyst systems for a DMO/VGO feedstock blend application. Catalyst System A (Ni-W for both HT and HC), while Catalyst System B (Ni-Mo promoted by P for HT and Ni-W for HC). The performance of Catalyst System A was superior to Catalyst System B in terms of the following:

- The activity of Catalyst A was higher by ~20°C lower SOR temperature for this catalyst system, at the 75 wt. percentage target. This affects a longer cycle length for this catalyst and lower catalyst deactivation rate.
- Catalyst A was more selective for naphtha, but gave lower selectivity for kerosene and diesel, in spite of the lower temperature used to achieve the conversion level. The product distribution can be manipulated by operating optimizing the temperature of the hydrotreating and hydrocracking catalyst beds.
- Analysis of the spent hydrotreating catalysts showed loss in surface area and pore volume and increase in coke and metals.

RECOMMENDATIONS

The refiner should continue to use Catalyst A for its stable and active life, in spite of the lower diesel selectivity. The difficulty to obtain a suitable catalyst arises from the fact that DMO is processed in few refineries, thus incentive for catalyst manufacturers to develop a catalyst system is not economical. DMO hydrocracking is a unique problem, that it can cause deterioration in catalyst activity and stability due to its high carbon content. Cooperation between R&D catalyst manufacturers and refiners is needed to solve this problem by tailoring design of the catalyst system. One of the problems encountered with DMO, is the ability of the pretreatment catalyst to denitrogenate the feed, thus causing deactivation of the second stage catalyst and thus shortening the cycle length. Options include design of catalysts with high dispersion, controlled acidity, and optimized pore structure.

Table 5. Comparison of Properties for Pilot Plant Products Criterion Performance Guarantee

PARAMETER	UNITS ASTM	Catalyst System A	Catalyst System B
C5-85°C, Light Naphtha			
Specific gravity @15°C	D-4052	0.6804	0.6796
g/cm ³	D-2887		
RON Clear	D-5134		
85-185°C, Heavy Naphtha			
Specific gravity @15°C	D-4052	0.7660	0.7625
g/cm ³	D-2887		
Sulfur, PPM	D-5453		
P/N/A, vol. %			48/38/8
185-240°C, Kerosene			
Specific gravity @15°C,	D-4052	1.8257	0.8134
g/cm ³	D-2887		
Sulfur, PPM	D-5453	35	96
Smoke point, mm	D-1322	20	22
Freeze point, °C	D-2386	<-95	-70
Aromatics, vol. %	D-1319	24	11
240-315°C, Light Diesel			
Specific gravity @15°C,	D-4052	0.8314	0.8218
g/cm ³	D-2887		
Sulfur, PPM	D-5453	124	153
Cloud point, °C	D-2500	-33	-35.6
315-375°C, Heavy Diesel			
Specific gravity @15°	D-4052	0.8378	0.8296
g/cm ³	D-2887		
Sulfur, PPM	D-5453	255	138
Cloud point, °C	D-2500	6.1	-0.6
Cetane Index	D-976	60.3	63.2
185-375°C, Distillate			
Specific gravity @15°, g/cm ³	D-4052	0.8303	0.8207
	D-2887		
Sulfur, PPM	D-5453	117	123
Flash point, °C		83	83
Cloud point, °C	D-2500	-16.1.	-17.2
Cetane Index		50.0	54
ASTM 85%	°C	314	316
375°C+, Residue			
Specific gravity @15°C		0.8751	0.8581
Sulfur	PPM	812	216
Kin. Viscosity @ 50°C	CSt	45.6	26.5

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