

HYDROCRACKING IN STATIC AND EBULATING BED REACTOR SYSTEMS

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Abstract

The results of hydrocracking of coal and petroleum oils in static and ebulating bed reactors are presented. The static bed system was found to be more efficient at low space velocities, while the efficiency of both the systems was almost the same at higher space velocities with respect to the yield of naphtha. The gas oil and coal oil hydrocracking severities, respectively, varied from 0.03 to 0.4 and 0.08 to 0.45 in the case of the static bed system and 0.03 to 0.31 and 0.07 to 0.32 in the case of the ebulating bed system. The static bed system affected more desulfurization, denitrogenation, and deoxygenation at lower space velocities, while the ebulating bed system was more efficient at higher space velocities. The static bed system appears to be more suitable for operations designed for the production of naphtha and for the complete removal of heterocyclic compounds.

Introduction

Hydrocracking of fuel oils is mostly carried out in static bed reactor systems which are very versatile for the processing of distillate oils. They, however, pose some problems in the treatment of heavy and residual oils. The residual oils may give rise to excessive deposits in the bed leading to catalyst deactivation, reactor plugging, and pressure drop in the bed. This necessitates frequent regeneration and changing of the catalyst which is an expensive and tedious problem. The heavy feed stocks can easily be processed in an ebulating bed type of reactor system as incorporated in the H-oil process (1, 2). In the ebulating bed system, the catalyst bed expands in excess of the true volume of the catalyst and the catalyst remains always in a state of random motion caused by the velocity of the feed oil, hydrogen, and some internal circulation of the oil. This system has several advantages and can be employed for the processing of different types of feed stocks ranging from vacuum residues to light gas oils (3, 4). It is, thus, evident that the ebulating bed system has the advantage of processing heavy and residual oils over the static system, while both the systems can be employed for the treatment of distillate oils of medium and low viscosities such as some gas oils and coal oils. There are no data available at this time in the open literature on the relative efficiencies of these two reactor systems for the processing of either petroleum or coal oil and is, therefore, difficult to select the proper system for practical adaptation. This communication describes the results of our investigation on the evaluation of the relative efficiencies of the static and ebulating bed reactor systems in the hydrocracking of petroleum and coal oil distillates.

Experimental

Materials.

The gas oil was prepared from a mixed base petroleum crude and the coal oil was obtained by the carbonization of a high volatile, bituminous coal from Utah at 650°C in a laboratory oven (Table I). A dual-functional catalyst containing sulfides of nickel and tungsten on silica-alumina in 1/16th-inch size pellets was used as the hydrocracking catalyst.

Equipment.

The static bed reactor system (Figure 1) contained a tubular 316-stainless steel reactor of 0.75-inch diameter and 40-inch length. One hundred c.c of the catalyst was used in the reactor. The ebulating bed reactor system (Figures 2 and 3) contained a reactor of 3-inch internal diameter and 9-inch height. The ebulation of the catalyst was mainly caused by a magnetic drive stirrer of 1800 r.p.m. The total volume of the catalyst bed was 500 c.c and 250 c.c of the catalyst was used for the experimental work.

Hydrocracking procedure.

Both systems were first flushed and pressurized with hydrogen and heated to the reaction temperature. The pressure was then adjusted to the experimental value and the oil was fed at the desired rate. The hydrocracking reactions were carried out at a constant pressure of 2000 p.s.i. and the hydrogen to oil feed ratio was maintained at about 1000. The data presented were obtained at a reaction temperature of 450°C unless otherwise mentioned. The values of space velocities varied in the range of $\pm 10\%$ and were rounded off. In the case of the static bed reactor, the experiments were carried out at 1 to 6 space velocities (V. of oil/hr./V. of catalyst). In the ebulating bed reactor system, experiments were carried out at 2.5 to 6 space velocities and the results were extrapolated down to 1-space velocity. Experiments could not be carried out at space velocities lower than 2.5 due to practical difficulties. In this system, the catalyst (250 c.c) expands to a total volume of 500 c.c (catalyst bed volume) and, hence, the space velocities were calculated on the basis of 500 c.c of the catalyst volume. The product was cooled in the condenser and the liquid product was collected in the separator. The gaseous product containing some uncondensed oil was passed through an active carbon tower to adsorb the oil and a gas meter to measure the rate and total volume passed. The liquid product was distilled and the fraction boiling up to 200°C was designated as naphtha and the residue as middle distillate. The yield of gas was calculated from the total gas and its composition. All products were obtained in single pass operations. The ratio of naphtha plus gas to the feed is designated as cracking severity. The analyses of the products were done by standard methods.

Results and Discussion

Selection of a suitable processing system mainly depends upon the type of feed stock to be processed and the nature of products desired. Due to the anticipated development of synthetic oil industry in the near future, feed stocks widely varying in physical and chemical properties will be available and

different types of processing systems may have to be employed for their treatment. It is, therefore, necessary to consider the different types of reactor systems available and evaluate their relative efficiencies for the processing of different feed stocks. A realistic evaluation can only be made by processing the same feed stock under similar reaction conditions in different systems. The gas oil and the coal oil used in this work were distillates of medium viscosity and can be easily processed in either static or ebulating bed system without problems, so that a reasonably good evaluation of the two processing systems can be made. The product distribution data obtained in the hydrocracking of gas oil (Figure 4) illustrated that both systems are almost equally efficient at space velocities greater than 4. They yielded almost the same amounts of naphtha and middle distillate at 430° and 450°C. The yield of naphtha, however, was very low and varied between 2 and 3%. Both systems exhibited different efficiencies at lower space velocities with respect to the yields of naphtha and middle distillate. At space velocities between 1.0 and 4.0, the static system yielded more naphtha and, correspondingly, less middle distillate when compared to the ebulating bed system. There was no significant difference in the yield of the gaseous product. The results obtained under the experimental conditions employed, indicate that the static bed system is more suitable for hydrocracking operations mainly designed for naphtha production, while both systems are equally suitable if middle distillate production is desired. This is further illustrated by the similar data obtained in the hydrocracking of a coal oil (Figure 5) which, however, yielded relatively more naphtha and less gas. The latter probably is due to the differences in the boiling ranges and the composition of the two feed stocks. The static bed system exhibited higher cracking severities when compared to the ebulating bed system at lower space velocities (Figure 6). The gas oil and coal oil hydrocracking severities, respectively, varied from 0.03 to 0.4 and 0.08 to 0.45 in the case of the static bed system and 0.03 to 0.31 and 0.07 to 0.32 in the case of the ebulating bed system. The results indicate that the product distribution obtained in the static bed system is being influenced very much by the space velocity, while the latter is not very critical in the case of the ebulating bed system. In any system the efficiency of contact between the catalyst and the reactants is mainly affected by the size of the catalyst and the space velocity. It appears that the space velocity is a more critical factor in the operation of the static bed system, while the size of the catalyst is probably more critical in the case of the ebulating bed system.

The product distribution at different levels of naphtha formation (Figures 7 and 8) indicates that both systems affect the product yields in a similar manner. The actual quantities, however, depend upon the nature of the feed stock. The properties of the naphtha and middle distillate produced by the two systems were found to be quite similar (Tables II and III). The coal oil naphtha was, however, more aromatic in nature than the gas oil naphtha. The composition of the gaseous product was somewhat different and the static system product from gas oil contained more C₄ hydrocarbons while the ebulating system product contained more C₁ and C₂ hydrocarbons. The static system product from coal oil contained more C₃ hydrocarbons, while the ebulating system product contained more C₁ and C₂ hydrocarbons. The production of more C₁ and C₂ gases in the ebulating bed system is indicative of the occurrence of more thermal cracking reactions in this system.

Removal of heterocyclic compounds from fuel oils is one of the major functions of hydrocracking and the extent of such hydroremoval depends upon the nature of the feed stocks, the catalyst, and the experimental conditions. The type of processing system may also have some influence. In gas oil hydrocracking, desulfurization and denitrogenation varied linearly with space velocity in the static bed system, while it was not the case in the ebulating bed system where the desulfurization and denitrogenation leveled off from a space velocity of 2 and down (Figure 9). The static bed system was more efficient for the removal of sulfur and nitrogen compounds at lower space velocities ranging from 1.0 to 3.0, while the ebulating bed system was more effective at higher space velocities ranging from 4.0 to 6.0. The efficiencies were almost the same in the range of 3 to 4 space velocities. Maximum desulfurization of 96% and denitrogenation of 83% were obtained in the static bed system at a space velocity of 1.0. In the case of the ebulating bed system, a maximum desulfurization of about 75% and denitrogenation of about 64% were obtained at a space velocity of 2.0. At space velocities lower than 2, there was no further removal of sulfur and nitrogen from the gas oil. It appears that the ebulating bed system is not very suitable for operations designed for complete removal of sulfur and nitrogen from fuel oils, though it can remove about 70 to 80%. The obvious choice, then, will be to employ the static bed system for such operations. Analogous results were obtained in the hydrocracking of the coal oil (Figure 10) wherein maximum desulfurization and denitrogenation of 97% and 87% were respectively affected by the static system and about 82% and 72% by the ebulating bed system. Oxygen removal from coal oil also followed the same pattern as the removal of sulfur and nitrogen. The rates of hydrocracking of sulfur, nitrogen, and oxygen compounds of gas oil and coal oil appear to be almost the same under conditions of high severities, irrespective of the type of processing system employed. The rates, however, were different under less severe conditions of hydrocracking (Figure 11). The material balance obtained in the two systems with gas oil and coal oil is given in Table IV. A total product recovery of about 102 to 103% was obtained, indicating 2 to 3% of hydrogen consumption in the process. The gas yield was approximated to about 0.5%. The yields of hydrogen sulfide, ammonia, and water were calculated from the extent of removal of sulfur, nitrogen, and oxygen during the process.

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Table I. Analysis of the feed materials.

	Coal oil	Petroleum oil
Gravity, °API	11.5	31.80
Sulfur, wt. %	0.84	0.94
Nitrogen, wt. %	0.92	0.80
Oxygen, wt. %	6.84	-
Distillation data		
I.B.P., °C	200	300
50% distillate, °C	305	340
F.B.P., °C	395	440
Hydrocarbon types, vol. % (neutral oil)		
Aromatics + olefins	68.0	29.0
Saturates	32.0	71.0

Table II. Properties of products of gas oil.
 Temperature: 450°C, pressure: 2000 p.s.i.,
 sp. vel.: 4.0

Products	Static bed	Ebulating bed
Naphtha		
Aromatics, vol. %	31.0	30.0
Saturates, vol. %	66.0	66.0
Olefins, vol. %	3.0	4.0
Sulfur, wt. %	0.14	0.21
Nitrogen, wt. %	0.18	0.26
Middle distillate		
Aromatics + olefins, vol. %	30.0	31.0
Saturates, vol. %	70.0	69.0
Diesel index	51.0	50.0
Gas, vol. %		
C ₁	10.0	15.0
C ₂	12.0	14.0
C ₃	29.0	28.0
C ₄	49.0	43.0

Table III. Properties of products of coal oil.
 Temperature: 450°C, pressure: 2000 p.s.i.,
 sp. vel.: 4.0

<u>Products</u>	<u>Static bed</u>	<u>Ebulating bed</u>
Naphtha		
Aromatics, vol. %	42.0	44.0
Saturates, vol. %	54.0	53.0
Olefins, vol. %	4.0	3.0
Sulfur, wt. %	0.11	0.13
Nitrogen, wt. %	0.21	0.28
Middle distillate		
Acids, vol. %	8.5	11.0
Bases, vol. %	1.0	1.7
Neutral oil, vol. %	90.0	89.0
Middle distillate (neutral)		
Aromatics + olefins, vol. %	61.0	60.0
Saturates, vol. %	39.0	40.0
Diesel index	41.0	41.0
Gas, vol. %		
C ₁	13.0	16.0
C ₂	15.0	19.0
C ₃	33.0	25.0
C ₄	39.0	40.0

Table IV. Material balance.
 Temperature: 450°C, pressure: 2000 p.s.i.,
 sp. vel.: 4.0

<u>Product yield,</u> <u>wt. %</u>	<u>Static bed system</u>		<u>Ebulating bed system</u>	
	<u>Gas oil</u>	<u>Coal oil</u>	<u>Gas oil</u>	<u>Coal oil</u>
Naphtha	5.0	10.0	4.0	9.0
Middle distillate	96.0	91.0	97.0	92.0
Gas	0.5	0.5	0.5	0.5
Water	-	1.0	-	1.0
Hydrogen sulfide	0.5	0.5	0.5	0.5
Ammonia	0.5	0.5	0.5	0.5