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Coal Hydrogenation and Bitumen Hydrocracking**

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Changes in Coal Particles During Simultaneous
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by

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When Athabasca bitumen is hydrocracked, coke and metals formed from compounds in the bitumen are deposited on the catalyst surface. This fouling and deactivation necessitate frequent catalyst replacement, which causes considerable operating expense. In an attempt to reduce the cost of catalyst replacement, studies in our laboratories have been directed at hydrocracking bitumen in the presence of coal particles, rather than conventional catalyst. It has been shown (1, 2) that the coal particles are able to accumulate metals and coke deposited from the bitumen. The objectionable material is thereby removed from the reaction system with the coal particles. The reaction conditions used for hydrocracking the bitumen also cause some hydrogenation of the coal. The purpose of this letter is to describe the changes which occurred to the coal particles while they were in the reactor.

The hydrocracking experiments were performed using a bench-scale fixed-bed reactor (3) having a volume of 155 ml and a length-to-diameter ratio of 12. Semi-anthracite coal (M=0.8, VM=13.4, Ash=7.8, FC=78.0) from Canmore, Alberta, or lignite (M=18.3, VM=35.6, Ash=10.2, FC=35.9) from Estevan, Saskatchewan in the form of 2.38 to 4.76 mm diameter particles (-4+8 mesh U.S. Standard Sieve Size) were placed in the reactor. Bitumen from the Alberta Oil Sands, described previously (1), and electrolytic hydrogen (purity = 99.9 wt %) flowed continuously into the bottom of the reactor and up through it. The product leaving the top of the reactor flowed to receiver vessels where the liquid and vapour were separated. Each experiment was performed at the following steady-state conditions for a period of 10.8 ks (3 hours): a pressure of $1.39 \times 10^7 \text{ N/m}^2$ (2000 psig), a temperature of 723 K, a bitumen volumetric space velocity of 0.278 ks^{-1} (1.0 hr^{-1}) based on an empty reactor, and a hydrogen flow rate of

0.0359 l/s at STP (5000 cf/Bbl). After the hydrocracking experiment, the solids were taken from the reactor, and the adhering oil was removed with toluene in a Soxhlet apparatus. Subsequently, the toluene was evaporated from the solids at room temperature.

Figure 1 shows the change in weight of coal solids with time, where time has been measured in terms of the number of experimental cycles. Each experimental cycle consisted of bringing the reactor and its contents up to the experimental conditions, maintaining the reaction conditions for 10.8 ks (3 hours), and bringing the system back to ambient conditions. The weight of solids is simultaneously decreased due to hydrogenation of coal and increased due to deposition of coke formed from compounds in the bitumen. It is apparent, from the data shown in Figure 1, that coal hydrogenation was the predominant process at the conditions used in these experiments. It is also clear that the weight reduction of lignite was much more rapid than that of semi-anthracite coal. The higher contents of moisture and volatile matter in the lignite may contribute to this phenomenon. In any event, this result is consistent with data obtained by hydrogenating coal in the absence of bitumen. For example, a summary prepared by Wu and Storch (4), shows that higher yields of gasoline and middle oil are obtained from low-rank coals than from high-rank coals.

Figure 2 shows that the size of the solid particles decreases with increasing reaction time. The largest change in size was observed after the first cycle. A much smaller change in particle size occurred between the first and later cycles. At comparable reaction times, the size of the lignite particles was generally smaller than that of the less reactive semi-anthracite coal particles. By combining the information in Figures 1 and 2, it is apparent that the total weight of solid phase material decreased, and that the material which did remain as solid phase particles become smaller in size as the reaction time increased. However, the reduction in particle size was not directly proportional to the decrease in solids weight as may be seen by comparing lignite particles after 4 cycles and semi-anthracite particles after 5 cycles.

The extent of coal hydrogenation and coke deposition reactions is indicated in Figure 3 as a function of the final particle size after one cycle. It has been assumed that the ash content of the particles remained essentially constant. Therefore, the ratio of fixed carbon to ash should be indicative of

the extent of reaction. The lignite particles initially had a 3.6 carbon to ash ratio. After reaction, the ratio was approximately 3.0 for the largest particles and 1.4 for the smallest. The decrease in fixed carbon/ash ratio with particle size may be due to the increase in particle surface/volume ratio. A larger surface area would permit a greater extent of reaction (in this case hydrogenation of coal). The results obtained with semi-anthracite coal (original fixed carbon to ash ratio = 10.0) are more complex. They suggest that coal hydrogenation predominates for the largest and smallest particles and that coke deposition predominates for the particles of intermediate size. A completely satisfactory explanation for the semi-anthracite results cannot be offered at the present time. However, there was one major difference between the two substances which should be noted. When lignite was used the particles removed from the reactor were non-porous. When semi-anthracite coal was used the particles were porous and resembled coke from low volatile bituminous coal (1). Coke formation from coal may have been at least partially responsible for the more complex results obtained with semi-anthracite.

The above data show that the design of the hydrocracking reactor will have a major effect on the extent of coal hydrogenation. For example, if a slurry reactor was used, bitumen and pulverized coal particles would be pumped continuously into the bottom of the reactor. Ideally, the particles should remain in the reactor long enough to maximize coal hydrogenation. Presumably this would be equivalent to the 1.4 fixed carbon/ash ratio shown for the smallest lignite particles in Figure 3. The other consideration is that when the particles become sufficiently small in size, the upward velocity of the liquid will exceed the terminal settling velocity of the particles and they will be swept out of the reactor. In principle, the upward velocity of liquid in the reactor can be chosen by appropriately matching the reactor diameter with the volumetric feedrate. A low enough liquid velocity would permit the particles to become sufficiently small, thereby maximizing coal hydrogenation, before they leave the reactor. It must be emphasized that coal hydrogenation is a secondary consideration. The primary objective is to accumulate coke and metals, formed from compounds in the bitumen, so that they will be removed from the reaction system with the particles. Coal hydrogenation is merely a desirable phenomenon which occurs simultaneously.

REFERENCES

1. Nandi, B.N., Ternan, M., Parsons, B.I., and Montgomery, D.S., Fuel (in press).
2. Ternan, M., and Parsons, B.I., "Hydrocracking Bitumen in the Presence of Coal - Experiments with Coals of Different Ranks". CANMET Scientific Bulletin, Department of Energy, Mines and Resources, Ottawa (1975).
3. Ternan, M., Nandi, B.N., and Parsons, B.I., "Hydrocracking Bitumen in the Presence of Coal - A Preliminary Study of Changes Occurring in the Coal", Mines Branch Research Report R-276, Department of Energy, Mines and Resources, Ottawa (1974).
4. Wu, W.R.K. and Storch, H.H., "Hydrogenation of Coal and Tar", U.S. Department of the Interior, Bulletin 633, (1968).

Figure 1 Weight Percent Solids Remaining in Reactor versus Number of Cycles (Reaction Time). Each experimental cycle consisted of bringing the reactor and its contents up to the experimental conditions, maintaining the experimental conditions for 10.8 ks (3 hours), and bringing the system back to ambient conditions.

Figure 2 Particle Size Distributions after Various Reaction Times. Weight Percent Undersize versus Particle Size.

Figure 3 Fixed Carbon to Ash Ratio versus Particle Size.





