

"NEW FUELS" VIA DIRECT COAL LIQUEFACTION

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INTRODUCTION

This paper is part of a series of papers (1-4) directed to inform the research community of the major achievements obtained during the development of the Integrated Two-Stage Liquefaction (ITSL) process and recent results from a few research laboratories which are closely related to the ITSL approach. The conclusion derived from these achievements is that the low-severity approach, exemplified by the ITSL process, has shaped a new direction in direct coal liquefaction development which needs further complementary support work of manifestly fundamental nature.

This paper intends to demonstrate that low-severity coal liquefaction operations are instrumental in producing some uniquely structured hydrocarbon distillate products. While the structure of these hydrocarbons can be traced to the unique condensed cyclic hydrocarbon structure present in coals, the low-severity operations, practiced in staged coal liquefaction processes, are the main contributors to the maintenance of the cyclic structure throughout and up to the final distillate products.

LOW-SEVERITY OPERATIONS

The ITSL and Chevron Two-Stage Coal Liquefaction processes have been described previously in detail (5-7) and they are representative of the novel low-severity staged operation approach which have shown to yield mostly reactive low-molecular-weight fragments (8). Other low-severity staged processes have been reported in the literature but bench-scale efforts were never conducted to a steady-state or a fully integrated operations, from which the required material and energy balances can be secured.

The staged process approach is based on the fact that there are two distinct paths - thermal and catalytic - to efficient coal liquefaction for obtaining "meaningful" fuel products and that the two must be separated because they have quite different, almost opposite, optimum operating conditions.

In the first stage coal and hydrogen donor solvent are reacted under hydrogen gas overpressure to form an "adduct" between coal and solvent. If the quality of the hydrogen donor solvent is excellent, as measured by proton NMR (9), practically no gaseous hydrogen is consumed and the resultant adduct contains exactly the arithmetic average of hydrogen available in the two components, i.e., solvent and coal mixed in a S/C ratio of 1.8 and containing 8.0-8.5 and 4.5-5.0 weight percent hydrogen, respectively, form an adduct with 6.5-7.2 weight percent hydrogen.

Since the best hydrogen donor solvent seems to be produced by "catalytic" hydrogenation at about 400°C in the ITSL second stage, the donor solvent is efficiently dehydrogenated in the "thermal" first stage at temperatures well above 400°C. No hydrogen loss from the donor solvent to gas phase is observed because of the hydrogen gas overpressure in the reactor.

The high temperature required in the thermal first stage serves also to convert efficiently coal preasphaltenes and asphaltenes to oils. It is fortunate that these conversions are very fast and the short reaction time provides the low-severity operations required to avoid retrogressive reactions. The optimum short contact time is of the order of 2-3 minutes, measured from the reactor inlet temperature of 320°C to the outlet at 440-450°C.

The coal extract produced in the first stage has been shown (6) to be more suitable than SRC I extract for the depolymerization occurring in the catalytic second stage. The low-severity operation in the second stage is maintained by limiting the reaction temperature at 400°C or below.

There are several reactions occurring in the catalytic second stage. The three most important are: 1. the hydrogenation of the solvent; 2. the removal of the heteroatoms, and 3. the depolymerization of the condensed aromatic compounds.

The requirements of this operation are to maximize the hydrogen donor quality of the recycle solvent and the removal of heteroatoms, while limiting the depolymerization to "controlled" ring opening without destroying the cyclic nature of the distillate ultimately produced. All these reactions have to be carried out with the minimum consumption of hydrogen and with a catalytic-bed reactors adsorbing about one million BTU per ton of coal processed owing to the highly exothermic hydrogenation reaction. Moreover, the required overall material balance involving hydrogen, recycle solvent and distillate product balances must be reached and maintained for a successful integrated continuous operation, even though there is a continuous declining catalyst activity.

Asking for all these required tasks to be accomplished in a single catalytic reactor seems to be asking the impossible. And yet by using an expanded catalytic bed reactor, similar to the commercial H-Oil reactor used in petroleum refineries, most of the task requirements are met.

On the other hand, there are many reactions occurring in the second stage which could be partially, if not totally, accomplished in the first stage, taking the workload away from the second stage. In the latter, more emphasis could be focused to produce better donor solvent and distillate product qualities. Of the total distillate coming out of the catalytic second stage the -343°C (-650°F) fraction, corresponding to the overhead fraction of the atmospheric flash distillation, was selected as the optimal product for being environmentally acceptable and already in the gasoline, diesel and jet fuel boiling range, as shown in Figure 1, and be upgraded to specification transportation fuels using modern commercial petroleum-processing technology.

Figure 1 shows typical distillation curves of several coal-derived oils compared to that of an Arabian-light petroleum crude. One notices significant differences between the ITSL distillate and the petroleum crude as well as the other coal liquids. In particular, the ITSL distillate contains a much larger middle distillate fraction (76 volume percent boils between 200° and 350°C), and less naphtha than coal-derived oils produced at higher-severity process conditions.

It is thought that this unique characteristic of the ITSL distillate supports the claim of being able to produce coal derived "New Fuels" that are significantly different from distillate derived from petroleum crudes.

The ITSL distillate has been refined successfully in a prototype refinery (10) using modern refining technology to produce specification transportation fuels with distinctive advantageous features, as will be described later.

NEW FUELS

Owing to the condensed cyclic structure of coal, the majority of the distillate products obviously will contain mostly condensed cyclic compounds, no matter what liquefaction approach is used. However, coal liquefaction at high-severity operations yield large quantities of light naphtha which, in most instances, contain above 45 volume percent of paraffins (11). Needless to say, converting condensed and non-condensed aromatics to paraffins requires the unnecessary consumption of hydrogen and is an indication of operations that are not optimally controlled.

On the other hand, low-severity liquefaction processes are able to depolymerize coals to low-molecular weight distillates that consist almost exclusively of cyclic compounds. To underline the importance of this extra-ordinary selectivity the enclosed table shows the product yield structure of the nominal boiling point to -350°C distillates produced by the ITSL process in which only mono- to condensed tri-cyclic compounds are present, no matter which type of coal is used, bituminous Illinois No. 6, Burning Star Mine or subbituminous Wyodak, South Pit Mine. Furthermore, one can observe that there are no condensed tetracyclics and, for the bituminous coal, no paraffins. It seems likely that the paraffins found in the distillate fraction of the subbituminous coal, probably were derived from the original structure of the coal, rather than being formed at low-severity operations. This assumption needs to be confirmed by a more precise characterization of the paraffinic species in the original coal and by monitoring their possible conversion to lower-molecular weight paraffins, either in the thermal or the catalytic stage of processing.

Figure 2 shows the comparative true boiling point curves of the ITSL atmospheric flash distillates from Wyodak and Illinois No. 6 coals, which reveals higher boiling compounds in the middle-distillate range for the Wyodak coal. The results were unexpected since subbituminous coal contains, on the average, lower molecular-weight condensed aromatic clusters and data from the H-Coal distillates from the same two coals have shown much lower boiling curves for Wyodak than for Illinois No. 6 coal (11). It should be noted that the H-Coal process operated at the same conditions for the two coals, whereas in the ITSL's catalytic second stage operations for Illinois No. 6 were conducted at 400°C and for the Wyodak coal at 370°C. From these results one might conclude that the distillate product yield distribution, in this case the condensed tri-bi and monocyclic ratios, can be

modified by changing processing conditions - a very desirable feature of controlled processing flexibility.

The fact that we can produce distillates from coal containing almost exclusively selected cyclic hydrocarbons, and can modify, under controlled conditions, their ratios within a selected boiling range is indeed one of the most important achievements in direct coal liquefaction R&D.

Another very important point is that these uniquely structured distillates have been characterized as "High Density Fuels," meaning that they provide greater energy per unit volume than do the more conventional fuels.

Figure 3 illustrates the selective conversion of coal to mostly bicyclic compounds such as naphthalenes, tetralins and decalins, representing about 50 percent of the total aromatics, hydroaromatics and naphthenes produced at low-severity operations, respectively. These "High Density Fuels" have different properties than petroleum-derived transportation fuels and can be considered as "New Fuels" with potential new applications. In addition, to provide desirable "more mileage per gallon fuels" and "lower freezing point" for jet fuels, these unique fuels can be produced at several levels of hydrogen to suit specific new engine requirements, and, possibly improve their performance.

Catalytic "hydrogenation" and "dehydrogenation" of these distillates require low activation energy of about 15 kcal/mole to produce, as desired, either naphthenes, or hydro-aromatics, or only aromatics, without breaking the original ring structure.

The versatility of the products as fuels can be appreciated if one notes the intrinsic properties of each of these products, whether they are condensed or non-condensed.

Naphthenes, upon heating prior to combustion, dehydrogenate to produce aromatics and large quantities of hydrogen providing a desirable strong "cooling" (endothermic) action in the precombustion zone. The mixture of hydrogen and aromatics is a highly desired fuel for recently developed high performance engines.

Hydroaromatics, alone, have never been tested as fuel. On the basis of their behaviour as "rapid hydrogen donors" in coal liquefaction they could provide hydrogen plus aromatics at a faster rate than naphthenes, if this would be a desirable feature.

Aromatics would provide higher combustion temperatures than naphthenes and hydroaromatics and could be suitable for newly introduced engines, i.e., ceramic engines, although soot formation problems need to be solved for this type of fuel. An all-aromatics fuel would be the least expensive to produce since it would require the least hydrogen addition in coal processing and refining steps.

CONCLUDING REMARKS

It is imperative to promote the development of these new fuels and eventually other forms of fuels from coal, presently in the exploratory research stage, by exploiting their unique properties.

They have the potential to create their own special fuel market aside from-- as well as in combination with--petroleum fuels.

Consequently, supportive funding for the development of new fuels from coal should not be negatively affected by the current low cost of petroleum.

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TRUE BOILING POINT DISTILLATIONS FOR ARABIAN LIGHT CRUDE, SHALE OIL AND COAL-DERIVED SYNCRUDES

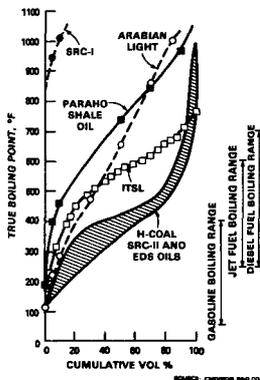


FIGURE 1

**ITSL DISTILLATE PRODUCTS
NOMINAL — 650°F**

	ILLINOIS NO 6 WOW 4998	WYODAK SGQ 9774
PARAFFINS	0.0	3.7
MONOCYCLICS	26.3	16.4
BICYCLICS	50.5	48.3
TRICYCLICS	21.6	29.5
TETRACYCLICS	0.0	0.0
TOTAL HYDROCARBONS	98.4	97.9

SOURCE: CHEVRON R&D CO.

**COMPARISON OF 725--750°F END POINT
WYODAK AND ILLINOIS ITSL OIL PILOT PLANT FEEDS
(ASTM D 2887 DISTILLATIONS)**

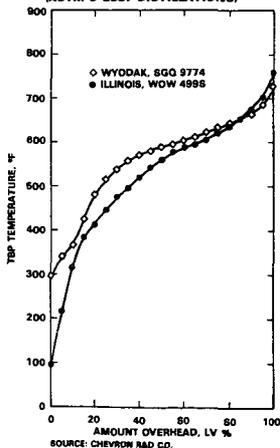


FIGURE 2

VERSATILE "NEW FUELS" FROM COAL

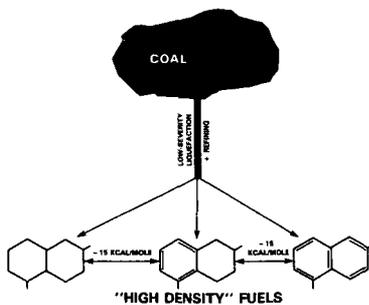


FIGURE 3