Effect of process parameters on the coprocessing of coal and heavy oils

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Abstract

The effect of process parameters on the combined coprocessing of coal and heavy residua was investigated. The kinetics of product distribution for the reaction of an Illinois No. 6 coal and two different residua was studied as a function of temperature and hydrogen pressure. The reaction products were separated by solvent fractionation into oils, asphaltenes, preasphaltenes and insoluble organic matter (IOM). The extraction process appears to be strongly dependent upon the asphaltene content of the solvent. At 450°C in the case of North Slope and at 425°C when Maya Crude was employed, the amount of IOM obtained increases with time due to retrograde reactions. With increasing severity, the yield of oils falls off, but the amount of asphaltenes and preasphaltenes in the THF soluble fraction decreases. Some interaction between coal and residuum reactions was detected from the comparison between hydropyrolysis and coprocessing runs.

INTRODUCTION

The depletion of light petroleum reserves and light oil production has forced refiners to process crudes containing a considerable amount of heavy ends. The politically controlled availability of the lighter Middle East petroleum, emphasizes the need for technology that provides greater flexibility in feedstock selection and processability. Moreover, the coprocessing of coal and petroleum residua or heavy bitumens offers a way of introducing the processing of coal into existing refineries without large plant capital cost.

In addition to these heavy bottoms, a high amount of naturally occurring heavy oil and shale oil is available throughout the world. The conversion of heavy oil and residua into distillate liquids by employing conventional petroleum catalytic cracking or hydrocracking technology is not straightforward. The processing of these materials at temperatures above 400°C leads to the formation of a substantial amount of coke. Furthermore, the heavy feedstocks

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contain large concentrations of inorganic elements such as nickel, vanadium and iron, which deposit on and poison the surface of the catalyst during upgrading.

Several direct liquefaction processes have been developed up to date. However, all of them require the employment of a high amount of recycle oil. Usually two-thirds of the liquid product has to be recycled to slurry the feed coal. The quality of the solvent is a critical factor affecting the extraction and upgrading process. It has been established that a liquefaction solvent must favour hydrogen-donation and hydrogen-transfer reactions [1–5]. It is also known that the physical properties of the solvent greatly influences the degree of coal solubilization [6].

The employment of heavy residua as solvents for coal liquefaction reduces the required recycle ratio. However, their paraffinic character makes them poor solvents for coal fragments [7]. Curtis and Cassel [8] found that the addition of tetralin, a good hydrogen donor, increases the production of benzene-soluble material under catalytic conditions. Clarke et al. [9] pointed out that saturated hydrocarbons have a detrimental effect on the extraction ability of a liquefaction solvent.

Rahimi et al. [10] showed that the degree of conversion of a subbituminous coal coprocessed with several crude derived petroleum residua in the presence of a low activity catalyst is not dependent on the content of the saturated fraction in the solvent. Moreover, they concluded that its (the solvent) hydrogen donor ability is not a determining factor affecting coal conversion.

Most of the work reported on coprocessing refers to catalytic processes and therefore the effect of the coal in promoting heavy oil upgrading has received much less attention [11]. The results available point towards a synergism between the heavy oil and coal or coal derived products [12,13]. The current work deals with the influence of process parameters on the coprocessing of coal and heavy residua. The effect of reaction time, temperature and hydrogen pressure on the product distribution obtained according to a solubility extraction scheme was evaluated. Some information about the mechanism of interaction between coal fragments and residua is outlined.

EXPERIMENTAL SECTION

Materials

North Slope ATB (+650°F) and Maya Crude ATB (+650°F), i.e. with boiling points above 340°C, were selected as petroleum solvents for this study. The analyses of the residua are presented in Table 1. Tetralin from Aldrich was also used as a solvent. The coal employed was a high-volatile C bituminous Illinois No. 6 pulverized to 100 mesh (150 μm), dried and kept in a vacuum

TABLE 1

Properties of petroleum residua

Property	North Slope ATB	Maya Crude ATB
Ultimate analysis (wt%)		
Carbon	85.5	84.7
Hydrogen	10.9	9.2
Nitrogen	0.6	0.7
Sulfur	2.3	4.9
Oxygen (by diff.)	0.7	0.5
Ash	<0.1	<0.1
Specific gravity (60°F)	0.961	1.008
Pentane insolubles (wt%)	3.9	19
Major metals (ppm)		
Nickel	22	71
Vanadium	39	370
Titanium	50	–
Iron	9	–

TABLE 2

Typical analyses of Illinois No. 6 coal

Proximate analysis (wt%)	Moisture	4.2 (as received)
	Volatile Matter	38.6
	Fixed carbon	50.3
	Ash	11.1
Ultimate analyses (wt%)	Carbon	70.2
	Hydrogen	4.8
	Nitrogen	0.9
	Sulfur	3.1
	Oxygen (by diff.)	9.9
	Ash	11.1
Heating value (Btu/lb)[a]	as received	11900
	moisture free	12450
	moisture ash free	14000
Real specific gravity		1.38
Sulfur forms	Sulfate	0.04
(wt%, m.a.f. basis)	Pyritic	1.36
	Organic	2.10

[a]1 Btu/lb ≅ 2.326 k J/kg.

desiccator before use. The analysis of a representative sample of the coal is shown in Table 2.

Apparatus and experimental procedure

Coal conversion experiments were carried out in a small batch tubbing bomb reactor [14] consisting of a stainless-steel Swagelok™ Tee-fitting (3/4 inch) sealed at both ends by Swagelok caps. The volume filled with gas and sample was about 25 cm³. A steel ball was introduced along with the reagents in order to enhance the agitation by a shaking system. A pressure transducer and a thermocouple were employed to measure reaction conditions. In the coprocessing reactions, the microreactor was charged with 2 g of moisture-free coal and 6 g of solvent accurately weighed. The vehicle-to-coal ratio was held constant. In hydropyrolysis runs 8 g of heavy oil were employed. The temperature was varied from 425°C to 475°C at 25°C intervals. Before each run, the microreactor was purged sequentially with nitrogen and hydrogen and then pressurized to 1000 psig (70 bar) of STP hydrogen. This led to a pressure ranging from 1500 to 2500 psig at reaction temperature. The microreactor was then introduced in a preheated fluidized sand bath maintained at the desired temperature. The time required by the microreactor to reach the reaction temperature was 1–2 min. Runs were performed at a reaction time varying from 0 to 60 min from the moment at which the reaction temperature was obtained. The data from the experiments at 0 min account for reaction taking place during the heating period.

Analysis of the products

After the reaction, the tubbing bombs were removed and quenched with water. Gas was vented and analyzed. The rest of the products were recovered and separated by solvent fractionation according to the PERC method [15]. The fractions obtained were the following: oils (pentane soluble), asphaltenes (toluene soluble and pentane insoluble), preasphaltenes (THF soluble and toluene insoluble) and an insoluble material that consists of insoluble organic matter (IOM) and ash. The IOM is quantified under the assumption that the weight of ash does not change during treatment.

RESULTS AND DISCUSSION

Hydropyrolysis of heavy oils

Figure 1 shows the effect of varying the initial hydrogen pressure on the hydropyrolysis of North Slope residuum at a temperature of 450°C and a 30 min reaction time. The product distribution indicates that the conversion of

asphaltenes increases with increasing hydrogen availability. At a cold hydrogen pressure of less than 1000 psig, the amount of toluene soluble–pentane insoluble material is greater than that corresponding to the raw product. The production of IOM due to coking-type reactions was seen to increase with increasing hydrogen pressure up to 1000 psig. Clearly, a hydrogen atmosphere is required to prevent retrogressive reactions to occur in the solvent.

The kinetics of North Slope hydropyrolysis was studied at 450°C. The product distribution for this set of runs is shown in Fig. 2. The IOM content of the product was seen to increase steadily with reaction time up to 10% at 60 min. In Fig. 3 a similar plot is presented for Maya Crude hydropyrolysis at temperatures of 425°C and 450°C. The asphaltene content of the products decreased with reaction time and the IOM increased up to 8% at 425°C and 16% at 450°C. From these experiments, it is apparent that the longer the residence
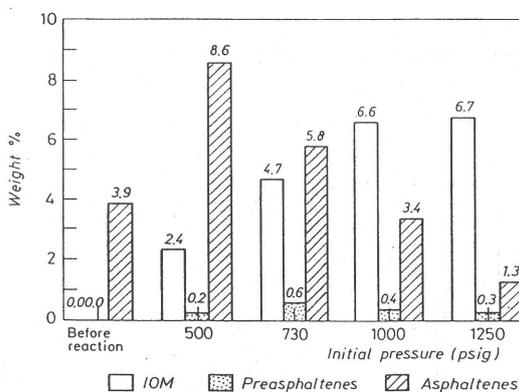
Fig. 1. Effect of initial hydrogen pressure on the products from hydropyrolysis of North Slope residuum. Temperature 450°C. Reaction time 30 min.
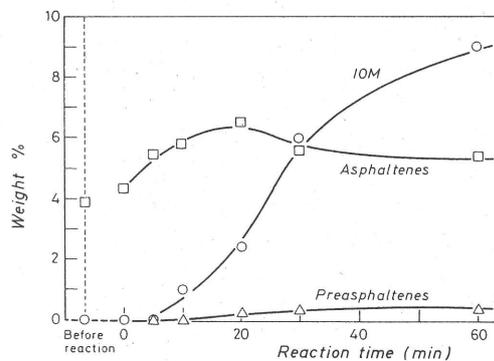

Fig. 2. Effect of reaction time on the product distribution from North Slope hydropyrolysis at 450°C. (IOM=Insoluble Organic Matter.)
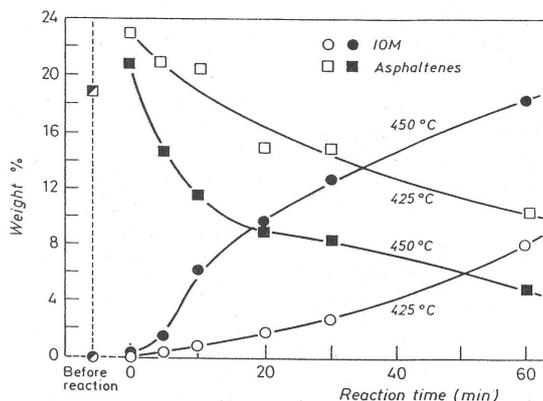
Fig. 3. Effect of reaction time on the product distribution from Maya Crude hydropyrolysis at 425 and 450°C.

time and the higher the temperature, the more IOM will be formed by reactions that lead to high molecular weight substances. The evolution of asphaltenes is controlled by a combination of two parallel reactions: their degradation to pentane soluble material and retrograde coke-forming processes. The differences in asphaltene reaction trends observed in Figs. 2 and 3 are due to the larger initial amount of asphaltenes in Maya Crude than in North Slope.

The importance of the availability of hydrogen in the retrogressive reactions in the solvent is shown by data reported before. From these data, it is apparent that condensation reactions leading to IOM are more important than those reported in other works. Curtis et al. [16] employed a 50 cm^3 microreactor and 9 g of sample in the hydropyrolysis of Maya Crude. Comparison with data presented in Fig. 3 reveals that the amount of IOM is more than ten times lower than that reported in our manuscript.

Coprocessing of North Slope/Maya Crude and Illinois No. 6

Figures, 4, 5 and 6 show the distribution of the products from the combined coprocessing of Illinois No. 6 and North Slope at temperatures of 425, 450 and 475°C. The yield of asphaltene and preasphaltene fractions decreases with time at all temperatures after a short induction period at the start of the process. The disappearance of these compounds was faster at higher temperatures. At a temperature of 425°C both the oil yield and coal conversion increased with reaction time. At 60 min, a conversion to THF soluble material corresponding to a solubilization of 65% of the initial m.a.f. coal was reached, but with increasing temperatures the amount of insoluble material increased with time, leading to a negative conversion.

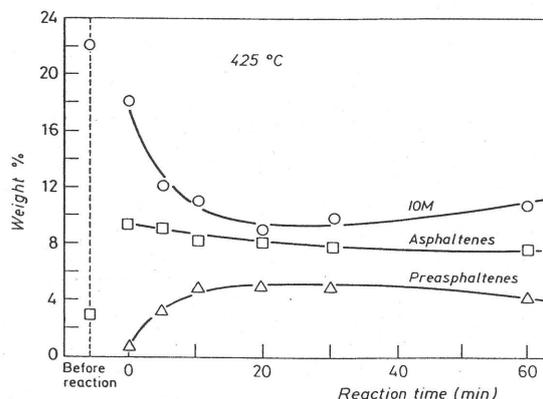In Figs. 7 and 8 the results from coprocessing of coal and Maya Crude at

Fig. 4. Effect of reaction time on the product distribution for the coprocessing of North Slope and Illinois No. 6 at 425°C. The weight percentage refers to all the products including gases and IOM.
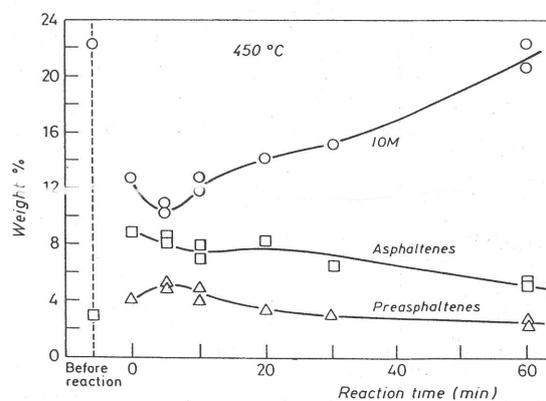

Fig. 5. Effect of reaction time on the product distribution for the coprocessing of North Slope and Illinois No. 6 at 450°C. The weight percentage refers to all the products including gases and IOM.

425°C and 450°C are presented. In this case, a greater amount of insoluble material from the solvent is produced with regard to the runs employing North Slope. The profiles obtained for soluble fractions are consistent with the higher density and molecular weight of Maya Crude. The initial asphaltene content of Maya Crude was almost five times greater than that corresponding to North Slope. This should lead to a higher rate of preasphaltenes and IOM formation. The kinetics of these retrogressive reactions has been described for donor solvent liquefaction by Moritomi et al. [17].

   The yield of oil and gases is presented in Fig. 9 for the experiments reported above. At higher temperatures the amount of soluble products tends to decrease with reaction time due to the occurrence of retrograde reactions. The picture for coprocessing runs is quite different from the product distribution
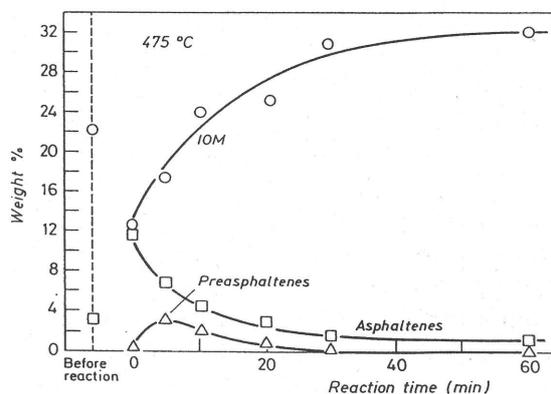
Fig. 6. Effect of reaction time on the product distribution for the coprocessing of North Slope and Illinois No. 6 at 475°C. The weight percentage refers to all the products including gases and IOM.
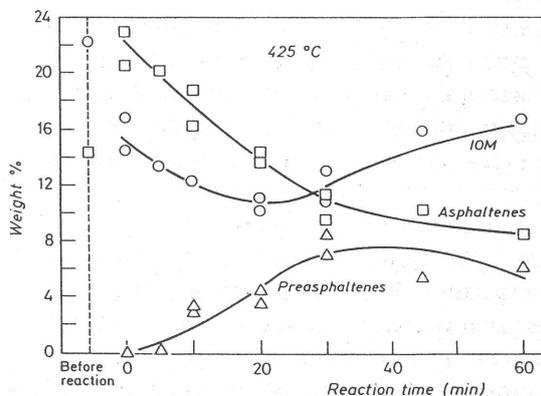

Fig. 7. Effect of reaction time on the product distribution for the coprocessing of Maya Crude and Illinois No. 6 at 425°C. The weight percentage refers to all the products including gases and IOM.

obtained in liquefaction of coal with a light donor solvent. In Fig. 10 the results of the liquefaction runs of Illinois No. 6 coal with tetralin are presented. The solvent-to-coal ratio was 3, the temperature 450°C and an initial S.T.P. hydrogen pressure of 1000 psig was employed.

In coprocessing, the heavy oil or petroleum residuum and the coal undergo simultaneous upgrading and conversion reactions. Because of the coke-forming character of the solvent, the conversion to THF soluble products is usually much shorter than the one corresponding to a liquefaction reaction. In Fig. 11, a comparison between observed conversion with a processing time of 10 min is provided for some coprocessing/liquefaction runs. As can be seen, for certain conditions a negative conversion was obtained. This does not mean, however, that the coal is not dissolved at all, but merely reflects the importance of rear-
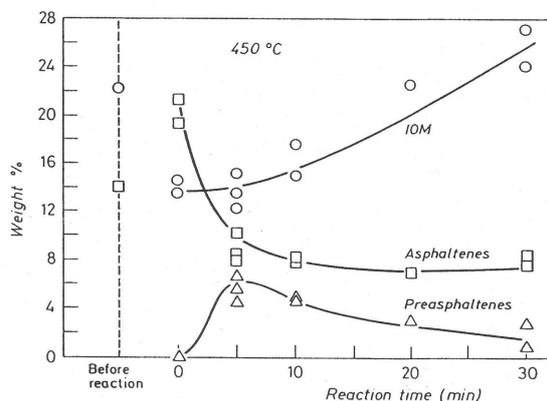
Fig. 8. Effect of reaction time on the product distribution for the coprocessing of Maya Crude and Illinois No. 6 at 450°C. The weight percentage refers to all the products including gases and IOM.
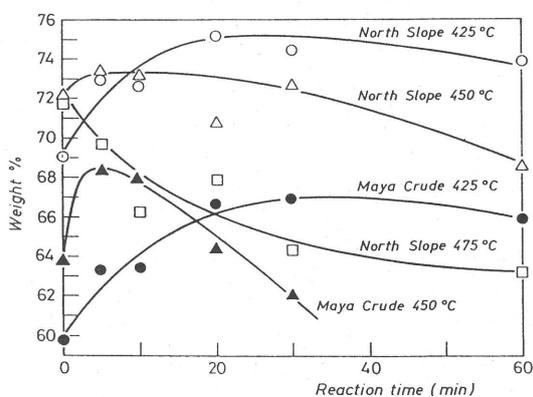

Fig. 9. Effect of reaction time on oil and gases production for coprocessing runs with North Slope and Maya Crude. The weight percentage refers to all the products including gases and IOM.

rangements in the solvent. Under the assumption that the reactions in coal and solvent are independent, the fraction of coal converted to soluble fractions (FCC) can be evaluated as a rough approximation by:

$$FCC = 1 - (IOM_c - IOM_h)/m.a.f. \text{ coal} \tag{1}$$

IOM_c is the insoluble organic matter obtained in a coprocessing run and IOM_h the amount of THF insoluble material originated by the hydropyrolysis of the solvent in the same conditions. In Fig. 12, some calculated conversions are presented. Even under this oversimplified assumption, the calculated conversion of coal ranges from 35 to 60% on a m.a.f. coal basis. In the absence of interaction, and assuming enough hydrogen is available, the evolution of the fraction of coal converted to products during a coprocessing reaction, should
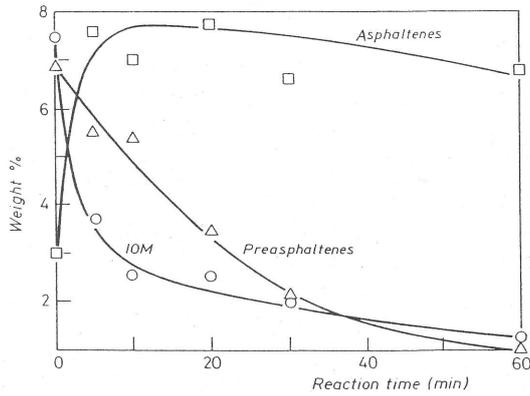
Fig. 10. Effect of reaction time on the product distribution for the liquefaction of Illinois No. 6 and tetralin at 450°C. The weight percentage refers to all the products including gases and IOM.
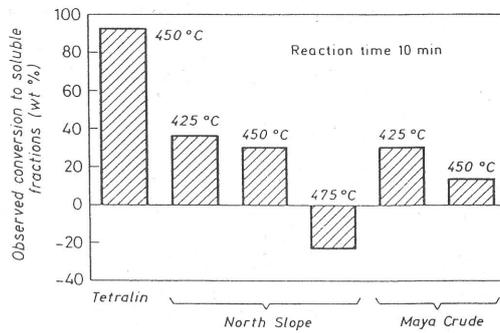

Fig. 11. Observed conversion of the coal-solvent system to THF soluble products in some liquefaction and coprocessing runs. Reaction time 10 min.
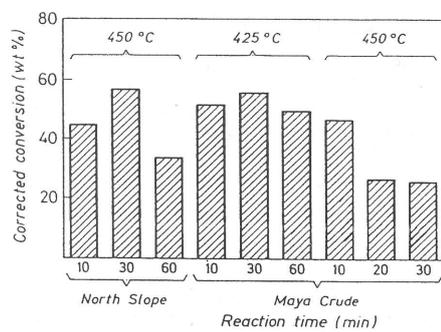

Fig. 12. Corrected conversion of coal to THF soluble products (FCC) under the assumption of independent behaviour of coal and heavy oil.

increase steadily with time. The coprocessing experiments indicate a fairly high conversion of coal, at least at the initial stage of the reaction at which more hydrogen is available (see initial part of IOM line in Figs. 4 to 8). Over a given contact time, which depends on the temperature of the treatment and the character of the solvent, the production of IOM was clearly stimulated by the presence of coal. The shortage of hydrogen and its preference for the aromatic coal dissolution products instead of the more paraffinic solvent might explain these results. Simultaneously a decrease in the amount of preasphaltene and asphaltene fractions was observed. This decrease was greater than expected in the absence of interaction. Some emphasis must be given to the fact that the solvent itself underwent changes leading to a conversion of asphaltenes and preasphaltenes into light products. For example, the coprocessing of coal and Maya Crude at 450°C favoured very much the production of IOM from the interaction between coal and solvent. However, even when the formation of insoluble products brought about an overall conversion of zero, the asphaltene content of the soluble fraction was about 9% (19% before reaction).

CONCLUSIONS

The extraction process is strongly dependent upon the nature of the solvent. To be more exact, it appears to be related with the amount of high molecular weight material contained in it. Some hydrogen donor substances, like partially hydrogenated aromatic hydrocarbons, are supposed to stabilize the radicals formed from coal by transfer of hydrogen incorporated from the gas phase. The observed behaviour of heavy oils was in good agreement with their low content in hydrogen donor compounds. In coprocessing reactions carried out above a certain temperature, the amount of IOM produced was greater than expected when assuming that the heavy oil upgrading reactions are independent of those of the coal. At the 450°C and 425°C in the case of North Slope and Maya Crude, respectively, the yield of IOM increased sharply after 20–30 min. The percentage of asphaltenes and preasphaltenes in the THF soluble fraction decreased with the severity of the treatment. Thus, the mechanism of interaction between the solvent and coal fragments must proceed in part via retrograde reactions leading to insoluble compounds. However, even in the absence of catalysts and hydrogen donors, a considerable amount of coal was converted, essentially to toluene insoluble products, at least at temperatures in the order of 425°C.

ACKNOWLEDGEMENTS

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