

KINETICS OF HYDROPROCESSING OF COAL-DERIVED VACUUM RESIDS

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Introduction

The direct liquefaction of coal produces a substantial amount of high boiling, non-distillable residuum, whose amount depends upon a number of factors such as the coal type, the hydrogen donor strength of the solvent, activity of the catalyst, and the conditions under which the direct liquefaction was run. Because of its high boiling point and potential thermal instability, this material is not suitable for processing in a conventional petroleum refinery. In a commercial liquefaction process as visualized today, therefore, this material would be recycled to the process to recover its energy value and to provide some of the solvent needed for the coal liquefaction process itself. Furthermore, this recycle oil has been shown to have a beneficial effect (i.e. increased oil yield) in the liquefaction process (1,2). Thus, it became important to determine the rates of conversion of these residual materials to products boiling in the fuel range (e.g. <850°F) and to know whether these high boilers will build up or be rapidly broken down in the recycling process. It was to follow the rates of resid breakdown (resid reactivity) under conditions approximating the conditions in the liquefaction process that this program was undertaken. Knowing the rates of resid condensation as well as breakdown are also important as retrograde processes reduce product yields and foul catalysts and equipment. This required the use of a reactor system capable of measuring hydroprocessing rates at very short contact times and the development of analytical methods for measuring the conversion and boiling ranges of the products. Resid conversion rates (both condensation and breakdown) would be correlated with composition data obtained by other analytical methods (e.g. TGA, NMR, elemental analysis etc.)

Experimental Section

Apparatus. The design and operation of the Short Contact Time Batch Reactor (SCTBR) system have been described in detail elsewhere (3). In operation, both the empty 30 cm³ reactor and the preheater and precooler are immersed in a fluidized sand bath and brought up to reaction temperature. High pressure hydrogen gas provided the driving force to deliver the reaction mixture of solvent, coal and catalyst from a blow case into the reactor at reaction temperature in of the order of 0.3 seconds, eliminating the heat up limitations in kinetic measurements. Discharging and quenching of the reaction mixture was carried out in the similar time frame. Hydrogen bubbled through the reactor from the bottom provided the necessary agitation. Temperature control was within $\pm 2^\circ\text{C}$. Reaction times as short as 5 seconds could be measured with considerable precision.

Materials Studied. Thirteen resid samples (boiling above 850°F) from coal liquefaction runs made at the Wilsonville pilot plant and two resid samples from Hydrocarbon Research Institute bench scale unit were prepared and supplied by CONSOL Inc. The feed coals for the resids produced at the Wilsonville pilot plant were Wyodak-Anderson, Illinois #6 and Pittsburgh coals. Selected properties, such as elemental analysis and the ¹³C NMR patterns obtained by CONSOL Inc., of each resid are shown in Table 1.

Resid Conversion Reactions. All reactions were run as mixtures of tetralin T (the donor solvent) and resid R over a range of T/R ratios, temperatures and catalyst. For each reactor run, 5 - 10 grams of resid were used together with added tetralin to make up the desired T/R ratio. Holdup of material prevented complete recovery of the reaction products. Recoveries varied from 75 to 85 wt%, depending upon the T/R ratio used. The determination of conversion and subsequent analytical results were therefore based on representative aliquots. Molybdenum naphthenate was used as the catalyst and was sulfided *in-situ* using methyldisulfide.

Reaction Product Workup Procedure. The reaction products were worked up by separating the solids from the liquids by filtration (Figure 1). The solid filter cake was washed with methylene chloride which went into the filtrate with the product liquids. The filtrate was then distilled at low temperatures (45°C) to remove the methylene chloride. The resulting solid cake and the filtrate were analyzed separately.

Analytical Methods - Conversion. The conversion to liquid was determined using thermogravimetric analysis (TGA) on the solid cake by an ash balance calculation.

The tetralin content of the methylene chloride-free filtrate was determined by gas chromatography using an added 1-methylnaphthalene internal standard.

To determine the amount of liquid product boiling above and below 850°F (454 °C), a

boiling range method, SimDis TG, was developed based on TGA (4).

The conversion of resid to the material boiling below 850 °F was estimated by Equation 1:

$$\text{Conversion} (< 850 \text{ }^\circ\text{F}) = \text{TSF} \times \left(1 - \frac{850 \text{ }^\circ\text{F}^*}{\text{RSF}}\right) \quad (1)$$

where TSF is the Tetralin Soluble Fraction of the resid (daf basis) determined by ash content in the solid resid after resid hydroprocessing; RSF is the Resid Soluble Fraction in tetralin and 850 °F* is the fraction boiling above 850 °F.

Analytical Methods - Resid Characterization. The resids studied were characterized by thermogravimetric analysis at 10°C/min in nitrogen from room temperature to 600 °C. This was followed by combustion of the remaining organic material at 100 °C/min to 850 °C in air. The derivative DTG curves, Volatile Matter (VM), Fixed Carbon (FC), and ash were determined. These TGA parameters as well as the peak temperatures and peak heights from the DTG curves are also included in Table 1.

Results and Discussion

As discussed in a previous section of this paper, conversion has been determined in part by an ash balance. Efforts to carry out hydroprocessing of resids using the Ni/Mo on alumina catalyst used in Wilsonville, however, resulted in unreliable conversions data because of the large amount of ash in the catalyst. In addition, it was found that the supported catalyst changed as the hydroprocessing progressed, making the calculations of conversion unreliable. Sulfided molybdenum catalyst, on the other hand, contributed little ash (which can be corrected for) to the system and gave very reproducible results. Preliminary experiments using a range of sulfided molybdenum naphthenate catalyst concentrations from 0.9 wt% to 5.0 wt% showed that 0.9 wt% catalyst resulted in only a barely detectable increase in conversion over uncatalyzed runs. However, 3 to 5 wt% (based on the resid) gave significant conversion to lower boiling products.

After considerable experimentation to determine appropriate reaction conditions, all 15 resids were hydroprocessed for 30 minutes at 420°C in 3 to 1 tetralin to resid weight ratio and 1500 psig hydrogen with and without sulfided molybdenum naphthenate catalyst (as 3 wt% molybdenum based on the resid charged). Each resid was also run at ambient temperature for comparative purposes.

Tables 2 and 3 show the conversions to material boiling below 850°F for the thermal and catalyzed hydroprocessed resids, respectively. It is to be noted that significant conversion to lower boiling material occurs even in the absence of catalyst. However, in the presence of the molybdenum catalyst, conversion to the lower boiling material was at least doubled. To attain as much as 30 to 40% conversion requires a significant amount of catalyst.

As Tables 2 and 3 show, there is considerable variation among the resids in terms of their reactivity and convertability to lower boiling products. Plots of the thermal and catalyzed conversions of the resids vs the feed coal types are shown in Figure 2. In the thermal hydroprocessing, there appears to be a correlation with the coal type used in the liquefaction, i.e., the lower rank coal produced resid which gave higher conversion on hydroprocessing in the absence of catalyst. On the other hand, if a catalyst is used, the resids from the three coals studied showed little or no difference in conversion under the conditions used. It will be noted in Figure 3 and Tables 1, 2 and 3 that those resids having high DTG peaks and high aromatic carbon content (by ¹³C NMR) generally show low conversions under the thermal hydroprocessing conditions while lower aromatic carbon containing resids show higher conversions in thermal hydroprocessing. Use of a strong catalyst apparently compensates in part for the high aromaticity.

SimDis TGA on the solid filter cake showed that, whereas there is considerable solubility of the resid in tetralin, up to 80 wt%, the solids themselves are not degraded to lower boiling material. Therefore, the resid must be solubilized in the recycle solvent for the resid breakdown to occur.

Summary and Conclusions

With the appropriate catalyst and conditions approximating coal liquefaction, high boiling coal-derived resids do break down to lower boiling products as they are recycled to the coal liquefaction process.

Coal-derived resids vary widely in their reactivity toward breakdown to lower boiling products under both thermal and catalytic conditions.

High catalyst activity appears to be necessary to convert these refractory materials to lower boiling materials.

Solubilization of the resid in the processing solvent is necessary for the molecular breakdown.

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Table 1. Selected properties of the resids

| Resid | Feed Coal | Number | Stream* | f_a | VM wt % | FC wt % | Ash wt % | T _{peak} C | Peak Height wt%/min (daf) |
|---------|--------------------------------------|--------|---------|-------|---------|---------|----------|---------------------|---------------------------|
| Resid L | Wyodak-Anderson Black Thunder | 4 | V 1067 | 34.0 | 51.3 | 48.7 | 19.1 | 470.7 | 4.59 |
| Resid K | | 5 | R 1235 | 24.6 | 53.6 | 46.4 | 17.2 | 464.8 | 4.60 |
| Resid H | | 6 | V 131B | 33.3 | 57.1 | 42.9 | 15.2 | 475.3 | 4.67 |
| Resid F | | 10 | V 1067 | 24.3 | 55.2 | 44.8 | 17.5 | 461.5 | 4.36 |
| Resid E | | 11 | R 1235 | 26.0 | 53.4 | 46.6 | 15.6 | 454.4 | 4.24 |
| Resid G | | 12 | V 131B | 25.9 | 55.7 | 44.3 | 15.9 | 462.2 | 5.02 |
| Resid I | Illinois No. 6 Burning Star No. 2 | 7 | V 1067 | 30.4 | 61.5 | 38.5 | 15.9 | 480.1 | 6.44 |
| Resid M | | 8 | R 1235 | 29.4 | 59.7 | 40.3 | 13.7 | 481.8 | 6.16 |
| Resid D | | 9 | V 131B | 29.2 | 70.9 | 29.1 | 9.9 | 490.5 | 6.83 |
| Resid J | Pittsburgh Ireland | 1 | V 1067 | 31.6 | 57.6 | 42.4 | 10.2 | 490.1 | 7.20 |
| Resid B | | 2 | R 1235 | 33.3 | 61.1 | 38.9 | 8.7 | 493.6 | 7.43 |
| Resid C | | 3 | V 131B | 31.5 | 61.0 | 39.0 | 8.5 | 490.2 | 6.23 |
| Resid A | | | | 38.9 | 51.8 | 48.2 | 17.0 | 472.1 | 4.75 |
| Resid N | | | | 20.6 | | | 0.4 | | |
| Resid O | | | | 18.8 | | | 4.1 | | |

*

V 1067 = interstage stream

R 1235 = 2nd stage product stream

V 131B = recycle stream

Table 2 Conversion of thermal hydroprocessing of resid

| Sample | Resid Name | Solid Residue | | Liquid Residue | | Conversion to 850 F- | | |
|--|------------------|---------------|------|----------------|------|----------------------|--------|------|
| | | Ash | TSF | Tetralin | SRF | | 850 F+ | |
| Resid A | W258V-131B | 17.0 | 50.1 | 79.7 | 88.2 | 11.8 | 9.6 | 15.0 |
| Resid B | W259R-1235 | 8.7 | 33.5 | 81.0 | 88.0 | 12.0 | 9.6 | 15.9 |
| Resid C | W259V-131B | 8.5 | 35.0 | 82.7 | 86.2 | 13.8 | 10.8 | 17.7 |
| Resid D | W261V-131B | 9.9 | 45.8 | 87.1 | 87.9 | 12.1 | 9.7 | 17.1 |
| Resid E | W262R-1235 | 15.6 | 43.5 | 76.0 | 88.4 | 11.6 | 8.6 | 19.6 |
| Resid F | W262V-1067 | 17.5 | 47.8 | 76.9 | 87.4 | 12.6 | 9.7 | 17.7 |
| Resid G | W262V-131B | 15.9 | 46.5 | 78.3 | 88.7 | 11.3 | 8.7 | 18.2 |
| Resid H | W260V-131B | 15.2 | 46.6 | 79.5 | 87.7 | 12.3 | 9.0 | 21.3 |
| Resid I | W261V-1067 | 15.9 | 50.8 | 81.8 | 88.9 | 11.1 | 8.5 | 19.4 |
| Resid J | W259V-1067 | 10.2 | 38.7 | 82.0 | 86.4 | 13.6 | 11.5 | 12.9 |
| Resid K | W260R-1235 | 17.2 | 49.0 | 78.4 | 86.9 | 13.1 | 9.8 | 19.7 |
| Resid L | W260V-1067 | 19.1 | 51.3 | 77.6 | 89.2 | 10.8 | 8.3 | 17.8 |
| Resid M | W261R-1235 | 13.7 | 45.6 | 81.1 | 90.1 | 9.9 | 7.9 | 16.0 |
| Resid N | HTI POC-01, O-43 | 0.4 | 33.0 | 99.2 | 80.6 | 19.4 | 14.1 | 27.0 |
| Resid O | HTI POC-02, O-43 | 4.1 | 38.0 | 93.1 | 70.6 | 29.4 | 22.4 | 22.1 |
| Thermal: 420 C; 30 min; 1500 psig H2 | | | | | | | | |
| Catalytic: 420 C; 30 min; 1500 psig H2; 3 wt% Mo | | | | | | | | |
| Control: 25 C; 10 min; 1500 psig H2 | | | | | | | | |
| TSF: Tetralin Soluble Fraction of resid, wt% (daf basis) | | | | | | | | |
| RSF: Resid Soluble Fraction in tetralin, wt% | | | | | | | | |
| 850 F+: fraction of boiling above 850 F | | | | | | | | |

Table 3 Conversion of catalytic hydroprocessing of resid

| Sample | Resid | | Solid Residue | | | Liquid Residue | | Conversion |
|--|------------------|------|---------------|------|----------|----------------|--------|------------|
| | Name | Ash | Ash | SF | Tetrafin | SR in Tetrafin | 850 F+ | |
| Resid A | W258V-131B | 17.0 | 51.5 | 80.7 | 82.5 | 17.5 | 9.9 | 35.0 |
| Resid B | W259R-1235 | 8.7 | 40.0 | 85.6 | 79.8 | 20.2 | 11.2 | 38.1 |
| Resid C | W259V-131B | 8.5 | 41.4 | 86.8 | 81.4 | 18.6 | 11.5 | 33.1 |
| Resid D | W261V-131B | 9.9 | 54.9 | 91.0 | 77.9 | 22.1 | 14.1 | 32.9 |
| Resid E | W262R-1235 | 15.6 | 44.2 | 76.6 | 80.6 | 19.4 | 11.3 | 32.1 |
| Resid F | W262V-1067 | 17.5 | 49.4 | 78.3 | 79.6 | 20.4 | 10.7 | 37.4 |
| Resid G | W262V-131B | 15.9 | 48.3 | 79.8 | 79.2 | 20.8 | 11.5 | 35.8 |
| Resid H | W260V-131B | 15.2 | 50.9 | 82.7 | 75.6 | 24.4 | 11.3 | 44.6 |
| Resid I | W261V-1067 | 15.9 | 56.6 | 85.5 | 76.2 | 23.8 | 11.9 | 42.7 |
| Resid J | W259V-1067 | 10.2 | 43.8 | 85.4 | 76.5 | 23.5 | 11.9 | 42.1 |
| Resid K | W260R-1235 | 17.2 | 52.1 | 80.8 | 78.1 | 21.9 | 12.4 | 35.2 |
| Resid L | W260V-1067 | 19.1 | 53.5 | 79.5 | 79.1 | 20.9 | 11.7 | 35.0 |
| Resid M | W261R-1235 | 13.7 | 53.7 | 86.3 | 80.2 | 19.8 | 11.7 | 35.3 |
| Resid N | HTI POC-01, O-43 | 0.4 | 36.4 | 99.3 | 67.9 | 32.1 | 16.7 | 47.6 |
| Resid O | HTI POC-02, O-43 | 4.1 | 48.3 | 95.4 | 70.2 | 29.8 | 19.1 | 34.3 |
| Thermal: 420 C; 30 min; 1500 psig H2 | | | | | | | | |
| Catalytic: 420 C; 30 min; 1500 psig H2; 3 wt% Mo | | | | | | | | |
| Control: 25 C; 10 min; 1500 psig H2 | | | | | | | | |
| TSF: Tetrafin Soluble Fraction, wt% (daf basis) | | | | | | | | |
| RSF: Resid Soluble Fraction in tetrafin, wt% | | | | | | | | |
| 850 F+: fraction of boiling above 850 F | | | | | | | | |

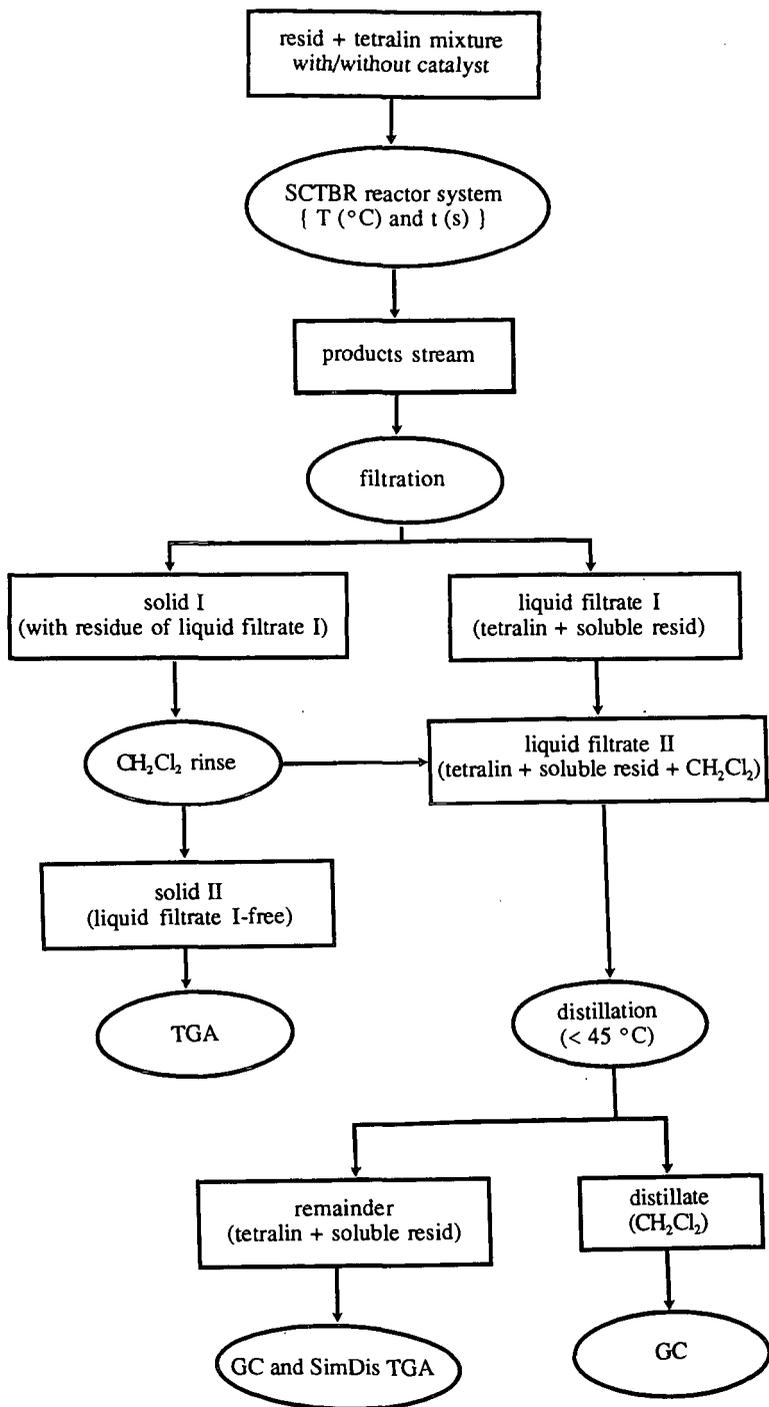


Figure 1 Scheme of the reaction product workup procedure

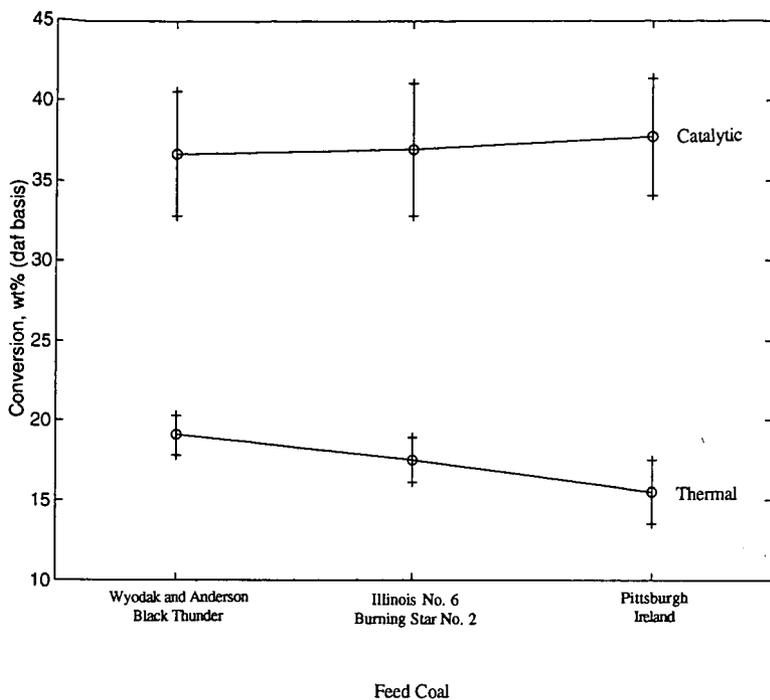


Figure 2 Thermal and catalyzed hydroprocessing conversions of the resids vs feed coal type

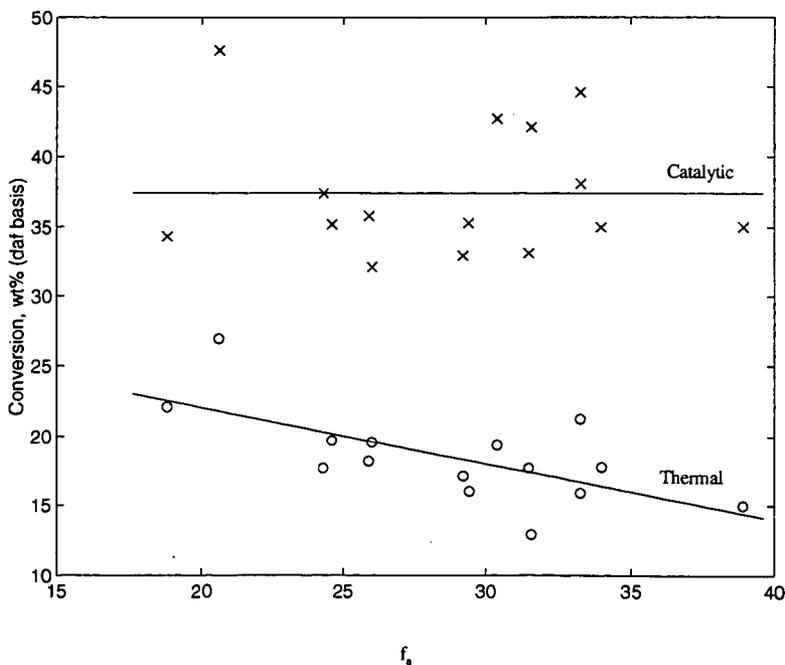


Figure 3 Thermal and catalyzed hydroprocessing conversions vs f_a of the resids