

CONVERSION OF RESID COMPONENTS IN CC-ITSL PROCESSING AT WILSONVILLE

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INTRODUCTION

Integrated Two-Stage Liquefaction technology has evolved to its current configuration, in which high recycle rates of solids and non-distillable materials contribute to high conversions and distillate yields. At the Wilsonville, Alabama, 6 ton/day pilot plant, the feed stream contains 29-33 wt % coal, 27-34 wt % resid (850°F⁺), and 8-16 wt % cresol insolubles (CI). Only 25-28% of the feed is distillable. In a recent assessment of analytical needs,¹ it was concluded that the chemistry of residual materials is an important area for study, including improved analytical methods for resid characterization and more extensive kinetic modeling. CONSOL has characterized process oils from each of the last nineteen Wilsonville runs; Close-Coupled Integrated Two-Stage Liquefaction (CC-ITSL) operation of the plant spanned fifteen runs since 1985. This paper represents an initial attempt to review and refine some areas of our investigations of resid conversion chemistry in Wilsonville runs.

EXPERIMENTAL

The experimental methods used in the analysis of whole process oils were reported elsewhere in detail.^{2,4} A brief description is provided here. Each whole process oil is distilled to 850°F to produce a distillate and a resid. Tetrahydrofuran (THF) solubles are obtained by repeated washing of distillation bottoms with distilled THF and recovery by rotary evaporation. Phenolic -OH concentration in the THF-soluble resid is determined by Fourier Transform infrared spectroscopy in THF solution. The THF-soluble resid is fractionated successively into oils (hexane-solubles), asphaltenes (benzene-solubles), and preasphaltenes (pyridine-solubles) with analytical quantitation by flame ionization detection (using different response factors for each feed coal represented). Each insoluble resid fraction is ashed at 800°C to constant weight and insoluble organic matter (IOM, also referred to as unconverted coal, or UC) is determined by difference between weights of ash and THF-insolubles.

The process oils analyses are used to calculate conversions (forced ash balance method) of the 850°F⁺ material and its various components in each reactor stage. The 850°F⁺ conversions are used to calculate conversion rate constants, conversion activities, and a catalyst deactivation rate constant.⁵ Equations used are:

$$C = \text{Conversion} = \left(\frac{850^{\circ}\text{F}^+ \ln/\text{Ash In} - 850^{\circ}\text{F}^+ \text{Out}/\text{Ash Out}}{850^{\circ}\text{F}^+ \ln/\text{Ash In}} \right) \times 100\%$$

$$K = \text{Rate Constant} = \text{WHSV} \left(\frac{C}{100 - C} \right)$$

$$A = \text{Conversion Activity} = K_0 E_{\text{act}} / RT$$

where E_{act} is assumed to be 23,500 cal/mol. In addition to conversion of the total 850°F⁺ resid, it is possible to calculate conversion of any component, including IOM, THF-solubles, oils, asphaltenes, preasphaltenes, and phenolic -OH.

RESULTS AND DISCUSSION

Background Table 1 summarizes the major operating conditions for CC-ITSL Runs 257 through 262. Generally several significant differences exist among runs. Detailed discussions of each run have been reported by Wilsonville⁶ and CONSOL⁷. A block diagram of the Wilsonville plant appears in Figure 1.

Comparison of CONSOL and Wilsonville Distillation Procedures and Resid Conversions. CONSOL uses an 850°F atmospheric equivalent distillation endpoint; the Wilsonville laboratory uses a 1050°F endpoint.⁵ Therefore, the 850 x 1050°F boiling fraction is considered resid in CONSOL's analyses, but distillate in Wilsonville's analyses. Table 2 illustrates this. On average, CONSOL typically measured about 14 wt % more resid than did Wilsonville. The amount of the difference may be related to reactor volume either directly or indirectly (see Table 2). Because of the difference, conversions calculated from CONSOL data are of 850°F⁺ material; Wilsonville's conversions are of 1050°F⁺ material. Some implications of this difference have been discussed elsewhere.⁵

One way to compare the (850°F⁺) conversions obtained by CONSOL with those obtained by Wilsonville (for 1050°F⁺) is to calculate the CONSOL/Wilsonville conversion ratio (R(C/W)) (Figure 2). Several observations were made from these data. First, R(C/W) averaged 0.8-1.0 in most runs, indicating CONSOL conversions were generally somewhat lower than Wilsonville conversions. Second, the R(C/W) ratio did not correlate with CONSOL and Wilsonville values for V-131B resid content (Table 2). Third, Run 262 was unprecedented in the low R(C/W), in each stage (not shown) and total system. It is not obvious why the 850 x 1050°F conversion was so low relative to the conversion of 1050°F⁺ material, but perhaps paraffinic components present in the 850 x 1050°F fraction were not readily converted to distillate in Run 262. Several points can be made regarding this: 1) Wilsonville found significant quantities of waxes in the Run 262 distillate products, and experienced unprecedented handling problems with them. 2) CONSOL found the heavy distillate paraffinity to be very high in Run 262. 3) The Run 262 resid alkyl beta protons were high, but not unprecedented; they were consistently this high only in one other CC-ITSL run (Run 257). How these results may be related to the use of Molyvan L (dispersed catalyst precursor first used in Run 262) is unknown. Perhaps dispersed Mo is not a good paraffin cracking catalyst, or the high coal space velocity during Run 262 was a contributor to poor cracking.

Corresponding first- and second-stage results are not shown, but are summarized here. R(C/W) for the first stage (typically slightly lower than one) in any given period is usually greater than that of the second stage (typically 0.8). These observations seem consistent with the first stage conversion which is dominated by IOM, and is not highly subject to variation in distillation conditions. The conversion of material in the second stage is more sensitive to distillation conditions and shows a greater difference in CONSOL and Wilsonville results. There was more scatter in the second-stage ratios.

Catalyst Deactivation in Run 258. Kinetic rate constants and activities (pre-exponential factors) for 850°F⁺ conversion were calculated for Run 258 material balance periods to evaluate catalyst activity and deactivation. In many recent runs, a look at catalyst deactivation was impossible because most operating periods were obtained at similar (equilibrium) catalyst ages. However, tests at several catalyst ages (some were from batch aging) in Run 258 allowed a catalyst activity evaluation. In order that the calculation would not be skewed by many data points near the equilibrated age of ca. 2500 lb (resid + C)/lb cat, all of those data (periods B through F, H, and I) were averaged to a single value (transitional periods were omitted). The deactivation rate constant is evaluated by considering the conversion activity, A, to have an exponential dependence on catalyst age, t, as $A = A' e^{-\alpha t}$, where A' is the initial conversion activity. As written, catalyst deactivation will result in negative values of α , the deactivation rate constant. The value of α was determined by regression of $\ln A$ on t. The results (Table 3 and Figure 3) indicate no significant effect of second-stage catalyst age on first-stage activity, as is expected for the thermal first stage (in the absence of any solvent donor effect). However, a deactivation rate constant is obtained for the second-stage catalyst with a high correlation, although for only four data points. The α and A' values for the second-stage catalyst are similar to those CONSOL found for Wilsonville Runs 250 through 257.⁵ However, the correlation of catalyst activity with age in Run 258 was much stronger than in those prior runs.

Conversion of Resid Components. Conversions of components of the 850°F⁺ resid (850°F⁺ resid, THF-solubles, oils, asphaltenes, preasphaltenes, and phenolic -OH) were calculated for Runs 257 through 262 (Figure 5). In Run 262 (Black Thunder coal, see Figure 5a), the resid + IOM conversion was positive in the first stage and low in the second stage, resulting in equivalent first-stage and total conversions. The conversion of THF-soluble resid and its components showed negative first-stage and total conversions, with higher second-stage conversions. The negative conversions represent gains in those components, from conversion of coal to solubles. Second-stage conversions of THF solubles, oils, and asphaltenes were approximately zero, making the corresponding first-stage and total conversions equivalent. Conversions of

preasphaltenes and phenolic -OH differ from those of the other components: they are greater in magnitude, showing greater first-stage and total gains (negative conversions); and the second-stage conversions are large and positive, resulting in increases in the total system conversions. The large negative conversion (net gain) of preasphaltenes in the first stage implies that preasphaltenes are primary coal solubilization products and that they are an intermediate form in the transition from coal to distillate. In the second stage, little additional coal is converted, and the conversion of preasphaltenes to other products is positive. The phenolic -OH conversion shows a similar trend with reactor stage, presumably because preasphaltenes are high in phenolic -OH (but the other fractions contain phenolics, as well). These results suggest that preasphaltenes and/or phenolic -OH could be important to include as a group in lumped kinetic modeling. This could be important in overall evaluations of performance, since heteroatom removal is a significant role of the catalyst, and since refining of the liquids to final products has a major impact on process economics.

Figure 5b shows the average results from Run 261, a catalytic/catalytic, low/high temperature run, with Illinois 6 feed coal. The preasphaltene and phenolic -OH conversions show the same trends as in Run 262. Trends in conversions of resid + IOM and other components somewhat resemble those in Run 262, but a number of differences are evident. In Run 261, the second-stage conversion of resid + IOM was relatively high and contributed a great deal to the total conversion. Conversions of THF-solubles and asphaltenes were positive in the second stage in Run 261, contributing to the respective total conversions. Total conversions of THF-solubles, oils and asphaltenes, and conversion of oils in each stage, were all close to zero. The results for Run 257 (another catalytic/catalytic Illinois 6 coal run) were very similar to those for Run 261, in spite of the fact that Run 257 used a high/low temperature configuration.

Resid component conversion results from two segments of Run 260 (Black Thunder coal) are shown in Figures 5c and 5d. One is thermal/catalytic, high/low operation (periods A-C), and the other is catalytic/thermal, low/high operation (periods D-F). The trends in resid component conversion during thermal/catalytic operation are quite similar to those seen in Run 261 (Figure 5b). Run 260 resembles the other subbituminous thermal/catalytic runs (262 and 258), however, in the relatively low second-stage resid + IOM conversion. That situation changed during catalytic/thermal operation in Run 260 (Figure 5d), when the two reactors more equally shared the contribution to conversion of resid + IOM. Also during catalytic/thermal operation, the first-stage, second-stage, and total conversions of most resid components were approximately zero. The preasphaltene conversions were still the most sensitive, but their magnitude was greatly reduced relative to the other runs discussed. The phenolic -OH conversions were quite small in magnitude, and were close to zero. Overall, it appears as if catalytic/thermal operation in Run 260 nearly balanced the work performed by each reactor and put the reactors into a near-equilibrium situation with respect to resid conversion. Thus, for most components, there was little net conversion or gain. A net conversion of coal to preasphaltenes occurred in the first stage and total system. In the second stage, coal conversion to resid was balanced by resid conversion to distillate.

CONCLUSIONS

In the latest Wilsonville CC-ITSL runs, the first stage primarily converts coal to solubles; conversion of soluble components takes place principally in the second stage. Preasphaltenes (which are high in phenolics) seem to be the primary coal solubilization product, and their conversion is effected primarily in the second stage. Including preasphaltenes and/or phenolic -OH components in lumped kinetic models may be useful, because defunctionalization and upgrading are important roles of catalytic reactor systems. Second-stage conversions of the oil and asphaltene components were typically low (relative to preasphaltenes conversions), and in many cases were close to zero. These results are consistent with the conventional wisdom regarding thermal/catalytic processing, in which solubilization and upgrading take place primarily in different stages, but appear to apply as well to catalytic/catalytic operation. Trends in resid component conversions in two catalytic/catalytic runs with the same feed coal (Runs 257 and 261) were very similar, in spite of a difference in temperature configuration (high/low vs. low/high). Catalytic/thermal operation in the last part of Run 260 seemed to balance the load in each reactor and result in a near-equilibrium situation with respect to resid conversion (little net conversion or gain of most resid components in either reactor). This situation was not typical of the other runs investigated (Runs 257-262).

Second-stage resid + IOM conversion activities in Run 258 material balance periods decreased significantly with catalyst age, indicating catalyst deactivation. The thermal first stage conversion activity showed no dependence on second-stage catalyst age.

The concentration of 850 x 1050°F material in the recycle oil seems to be influenced primarily by reactor volume in use, perhaps by changing the reactor dynamics (such as the relative thermal and catalytic reaction volumes). During Run 262, the 850°F+ conversion relative to 1050°F+ conversion was quite low in each stage, possibly due to the presence of paraffinic components not easily converted to final products.

RECOMMENDED FUTURE WORK

The resid conversion chemistry of Wilsonville runs prior to Run 257 should be explored in more detail and more-detailed analysis of runs after 257 may also be warranted. Calculation of kinetic rate constants and conversion activities for individual components (instead of only the resid + IOM) might also be of interest. Addition of one more analysis would make it possible to obtain conversions of various hydrogen (proton) types, perhaps providing additional information on the nature of the converted resid.

What more is needed in the future? Innovative kinetic modeling is needed, even for empirical yield and conversion data. For example, experience indicates that bituminous coal converts readily to soluble resid, but less readily to distillate. Conversion of subbituminous coal to solubles is more difficult, but the solubles are readily converted to distillate. An adequate model of liquefaction phenomena would have to account for differences in the coal and resid conversion kinetics in various coals. A comprehensive kinetic model (of proper reaction order) should include the following (preferably mathematically separable) terms: coal (separate terms for IOM and resid reactivity), catalyst (activity and deactivation susceptibility by various routes), and processing conditions (temperature, space velocity, resid concentration, coal and ash recycle concentration, etc.). Current models do not adequately separate processing condition effects from those of the coal and catalyst.

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Table 1. Conditions Used in Recent Wilsonville Runs

Condition	Wilsonville Run					
	257	258	259	260	261	262
Coal* (MF Ash Content, wt %)	BS 2 (11.3)	SC (5.6), BT (7.3)	Ire. (4.5), Ire. (14.9)	BT (6.2)	BS 2 (11.8)	BT (6.4)
Coal Feed Rate, MF lb/hr	166-531	193-293	230-356	251-352	357-548	242-346
Coal Concentration, MF wt %	30-34	30	30-33	30	29-33	30
Resid in Recycle Solvent, wt %	40-50	40-41	40-51	39-40	33-49	32-41
Solids in Recycle Solvent, wt %	12	20-25	6-13	20-21	11-12	19-20
Reactor Vol., % Stg 1/Stg 2	100/100, 50/50	50/50	50/50	100/75, 75/100	100/100	50/50
Catalyst Configuration	Cat/Cat	Th/Cat	Cat/Cat	Th/Cat, Cat/Th	Cat/Cat	Th/Cat, Th/Th
Temperature Configuration	High/Low	High/Low	High/Low	High/Low, Low/High	Low/High	High/Low
Interstage Separation	No	Yes	Yes	Varied	Yes	Yes
Temp. in Stage 1, °F	760-810	825-865	810-825	775-840	790-810	825
Temp. in Stage 2, °F	760-805	740-790	760-790	775-805	800-825	760-810
Stage 1 Catalyst**	Am 1C	None	Am 1C, Sh 324	None, Sh 324	EXP, Cr 324	None
Replace. Rate, lb/T MF Coal	0-3	-	0-4	0-3	0-3	-
Stage 2 Catalyst**	Am 1C	Sh 324	Am 1C, Sh 324	Sh 324, None	EXP, Cr 324	Cr 324, -
Replace. Rate, lb/T MF Coal	0-3	0-3	0-4	3, -	0-3	3, -
Thermal Stage Space Vel., lb MF Coal/hr/ft ³ , (C=Constant)	-	51C-78C	-	31C-43C	-	64C-92C
Catalytic Space Vel., lb feed/hr/lb cat.	3.7-6.7/ 3.7-7.0	-/3.6-5.7	1.8-6.8/ 1.7-6.5	-/3.1-3.9, 2.8-4.0/-	2.9-6.4/ 2.6-6.0	-/4.7-6.6, -/
Stage 1 Catalyst Age, lb (Resid+Solids)/lb cat.	926-2308	-	895-1918	1415-1497	1324-2812	-
Stage 2 Catalyst Age, lb (Resid+Solids)/lb cat.	727-2314	415-3452	718-2710	1330-1368	1090-2238	1315-1545
Slurry Catalyst and Feed Rate: Fe ₂ O ₃ , wt % MF Coal	0	2	0	2	0	2
Molybden L, Mo ppm of MF Coal	0	0	0	0	0	100-1000

Coals are: Black Thunder and Spring Creek (subbituminous), and Burning Star 2 and Ireland (bituminous).

**Catalysts are: Amocat 1C, Shell 324, Criterion 324, and EXP-AO-60.

Table 2. Comparison of CONSOL and Wilsonville Resid Concentrations in Wilsonville Pasting Solvent (V-131B)

Wilsonville Run	Reactor Volume Used, % (1st/2nd Stage)	Resid in V-131B Pasting Solvent, wt %		Fraction of 1050°F ⁺ in 850°F ⁺ (Wilsonville wt %/CONSOL wt %)
		Wilsonville	Difference (CONSOL-Wilsonville)	
Run 262	50/50	37.2 ±2.9	12.5 ±2.0	0.75 ±0.03
Run 261	100/100	43.3 ±6.7	18.5 ±3.5	0.70 ±0.07
Run 260	100/75 (A-C), 75/100 (D-F)	39.4 ±0.8	15.2 ±3.4	0.72 ±0.05
Run 259	50/50	47.4 ±4.1	13.4 ±1.7	0.78 ±0.02
Run 258	50/50	40.8 ±0.4	7.1 ±1.5	0.85 ±0.03
Run 257	100/100, 50/50	46.0 ±4.8	19.1 ±4.9	0.71 ±0.07
257A-257H	100/100	45.7 ±4.9	21.9 ±1.2	0.67 ±0.03
257I-257K	50/50	46.8 ±5.4	11.7 ±0.4	0.80 ±0.02

Table 3. Catalyst Deactivation Rate Calculation For Wilsonville Run 258

Period	Cat. Age, lb (Resid+Cl)/lb Cat.	First Stage A, 10 ⁷	Second Stage A, 10 ⁷
K	559	1.84	3.75
L	1130	1.36	2.22
M	1314	1.57	2.16
Equilibrated (Avg. B, C, D, E, F, H, I)	2523 ±84	1.81 ±0.43	1.05 ±0.61

First Stage: $\alpha = 0.30 \times 10^{-4}$, $\sigma(\alpha) = 1.17 \times 10^{-4}$, $A' = 1.56 \times 10^7$, $\sigma(A') = 1.18$, $R^2 = 0.03$
 Second Stage: $\alpha = -6.2 \times 10^{-4}$, $\sigma(\alpha) = 0.06 \times 10^{-4}$, $A' = 4.96 \times 10^7$, $\sigma(A') = 1.09$, $R^2 = 0.98$
 Note: Units of A' are lb total feed/hr/lb cat, units of α are lb Cat./lb (Resid + Cl).

