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NOVEL SUPPORTS FOR COAL LIQUEFACTION CATALYSTS

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by

Henry W. Haynes, Jr.

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Chemical Engineering Department
University of Wyoming
P. O. Box 3295, University Station
Laramie, Wyoming 82071

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ABSTRACT

Estimates of liquid circulation rates were obtained from an analysis of the cold model data and a plot of these values versus stirrer speed appears to be unique for the 60° axial impeller. The recycle ratio is typically of the order of 1000/1 or greater, and for all practical purposes the reactor may be treated as a perfectly mixed reactor.

The work up of hydrotreating Run PDJ03 is complete. The run was terminated prematurely due to a rupture disk failure, but eight of the ten planned balance periods were completed. Carbon material balances were slightly high, ranging from 100.7% to 106.7%. Reaction rates for hydrogen uptake, hydrodesulfurization and hydrodenitrogenation were calculated. The catalyst did not deactivate significantly for the duration of the run and no evidence of catalyst attrition was observed after 215 hours of service.

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INTRODUCTION

Catalyst deactivation is a severe problem in coal liquefaction applications. Generally speaking, catalysts deactivate with process time as a consequence of coke formation, metals and ash deposition and sintering. The evidence is suggestive of two type of coke deposition. During the early stages of liquefaction the chief culprit may be categorized as "Type I" coke formation. Many investigators have observed that coke builds up rapidly to levels sometimes exceeding 20 percent by weight, and that this buildup is accompanied by a sharp decrease in catalyst activity. After this initial period, the coke content of the catalyst remains nearly constant, and a scan of a "coke equilibrated" catalyst particle indicates that carbon is deposited uniformly throughout the pellet cross-section. Type I coke deposition is accompanied by a substantial reduction of pore volume in the micropore region and clogging of these fine pores is undoubtedly a major contributor to the deactivation. In some situations carbonaceous deposits will accumulate at the external surface of the catalyst particle. This "Type II" carbon deposition has been observed on spent coal liquefaction catalysts (1), and on catalysts that had seen service in the hydrotreatment of heavy coal liquids (2, 3). It appears that the critical factor is the presence of benzene (or toluene) insolubles. It is speculated that the Type II carbon deposits serve to plug external pores and to prevent access to the particle interior.

Metals and ash deposits also accumulate at the external surface of the catalyst particle as time progresses, and this leads to deactivation of the catalyst most probably via a pore plugging mechanism. The commonly deposited metals include Fe, Ti, Ca, B, Mg, Na, and Si. Concentrations of up to (and sometimes exceeding) five weight percent are

common. The analysis of spent catalysts from the Wilsonville facility revealed that the penetration depth can be quite substantial (4).

Sintering is reported to be a cause of deactivation in the H-Coal process (5). The effect is especially pronounced when low rank coals are processed, and the degree of sintering appears to be related to the presence of water in the reaction mixture. Thomas and Sample report a loss of catalytic metals--Mo, Ni and Co--from spent H-coal catalysts (6). Similar phenomena have been reported in commercial hydrodesulfurization processes.

The objectives of this research are first to construct a Catalytic Coal Liquefaction Microreactor (CCLM) and then to use this unit to screen catalysts prepared from novel and/or modified supports for coal liquefaction applications. Run lengths will be sufficient to give a measure of catalyst deactivation rate. Modified supports will include aluminas treated with alkali and alkaline earth metals and halogens. Novel supports will include carbons, single component oxides and composite oxides. Throughout this work, efforts will be made to correlate coking tendency with catalyst acidity measurements. While the emphasis of this investigation is not directed towards pore structure, the importance of this variable is not underestimated. Pore structures of all catalyst samples, both fresh and spent, will be monitored routinely.

ACCOMPLISHMENTS

The last quarter was devoted to the continuation of shakedown runs on the Catalytic Coal Liquefaction Microreactor (CCLM) in the hydrotreater mode of operation. The feed was a raw creosote oil (24-CB) obtained from Allied Chemical, and the catalyst was Amocat 1A (CoMo/Alumina). Feed and catalyst analyses were provided in the previous report (7). The catalyst was presulfided with a mixture of CS₂ in heavy mineral oil according to the standard procedure discussed in the last report. No coal paste was fed to the unit.

In addition, calculations were performed on the cold model data to obtain an estimate of circulation rate and the approach to perfect mixing in the reactor.

Estimation of Circulation Rate:

Estimates of the internal circulation rate as a function of stirrer speed were calculated from observations of the stirrer speed at incipient fluidization in the cold model. Only the spherical particle data were employed in this calculation since ample spherical particle data were available and this avoided the introduction of particle shape factors into the calculation. The data upon which these calculations are based are summarized in The 5th quarterly report (8).

Upon equating the drag force in a fixed bed of spheres to the displacement weight of the bed, the following equation is obtained for the incipient fluidization velocity:

$$1.75 Re^2 + 150(1 - \epsilon) Re - \epsilon^3 Ga = 0 \quad (1)$$

where

$$Re = \frac{u_i d_p \rho_f}{\mu_f} \quad (2)$$

$$Ga = \frac{d_p^3 (\rho_p - \rho_f) \rho_f g}{\mu_f^2} \quad (3)$$

and u_i is the superficial velocity at incipient fluidization, d_p is the particle diameter, ρ_f and ρ_p are the fluid and solid densities respectively, μ_f is the fluid viscosity, and g is the gravitational acceleration constant. In our calculations we have taken $\epsilon = 0.476$ for the porosity of a loose packing of spheres.

The stirrer speed at incipient fluidization, S_i , is observed experimentally for a given particle/fluid combination and the corresponding Reynolds No. is calculated from Eq. (1). The superficial incipient fluidization velocity is then calculated from Eq. (2), and multiplying by the bed cross-sectional area gives the liquid circulation rate.

Liquid circulation rates calculated in this manner are plotted versus stirrer speed in Figure 1. Interestingly, all the data for different fluids and particles fall on the same curve. This figure would therefore appear to have predictive capabilities over the range of fluid properties investigated.

We can now make a statement about the approach to perfect mixing or backmix behavior in the reactor. For a five gram catalyst charge and a Weight Hourly Space Velocity (WHSV) of 2, the feedrate to the reactor will be approximately 10 cc/hr. It is evident from Figure 1 that the ratio of circulation rate to feedrate, i.e. the recycle ratio, will be of the order of thousands provided that the stirrer speed is above about 600 rpm. To

Figure 1. Circulation Rate vs. Stirrer Speed, 60° Axial Impeller.

Figure 2. Reactor Temperature Program, Run PDJ03.

provide perspective, consider a first order irreversible reaction taking place in a recycle reactor operating at the 90% conversion level. At a recycle ratio of 100/1, the error introduced in the calculated first order rate constant by assuming perfect mixing is only 4.4%. At a 1000/1 recycle ratio the error is reduced to less than 0.5%. The errors are even less severe at lower conversion levels. Thus it would appear that the ebullated bed microreactor may be treated as a perfectly mixed reactor for practically all situations likely to be encountered.

Run PDJ-03:

This was to have been a 10 day run at $T = 750^{\circ}\text{F}$, $P = 2000$ psig, $\text{WHSV} = 2$, H_2 Treat Rate = 5000 SCF/BBL and a stirrer speed of 1500 rpm. On the morning following the 8th yield period, the rupture disk on the reactor blew forcing termination of the run. The rupture disk blew for no apparent reason as the unit was operating smoothly. The cause is believed to be the high operating temperature of the reactor and the fact that a 316 SS rupture disk was in use. Autoclave Engineers recommends that a nickel alloy rupture disk be installed for high temperature service.

The reactor temperature during presulfiding is plotted in Figure 2. A run summary for the eight balance periods is provided in Table 1. The carbon material balances tend to be a bit high for all yield periods, ranging from 100.7% to 106.7%. During yield period no. 4 the hose leaving the WTM was pinched and the reading may have been affected. Also, due to a valve switching error some depressuring of the second high pressure accumulator through the WTM occurred. This may explain the high material balance. This may also have occurred to a lesser extent during yield period 5. The consistently high material

Table 1
Run PDJ03, 5.0005 GMS Amocat 1A

Run Summary:

Yield Period No.	1	2	3	4	5
Yield Period Length, HR	6.0	6.0	6.0	6.0	6.0
Average Temperature, F	750	749	750	750	750
Average Temperature, C	399.0	398.6	399.0	398.7	399.0
Average Pressure, PSIG	2030	2020	2010	2000	2010
Liquid Feed Rate, GM/HR	9.55	10.12	10.27	9.85	10.25
Weight Hourly Space Velocity	1.91	2.02	2.05	1.97	2.05
Weight Hourly Space Time	.524	.494	.487	.508	.488
Hydrogen Treat Rate, L(STP)/HR	8.17	8.17	8.17	8.17	8.17
Hydrogen Treat Rate, SCF/BBL	5210	4920	4850	5050	4860
Stirrer Speed, rpm	1500	1500	1500	1500	1500
Exit Gas Rate, L(STP)/HR	4.58	4.86	4.8	6.03	5.98
Cumulative Hours on Catalyst	20.5	44.5	68.6	92.6	116.6
Cumulative Wt. Oil/Wt. Catalyst	42.5	91.6	140.5	190.3	239.0
Liquid Material Balance, Wt%	101.04	105.2	103.0	107.5	102.7
Carbon Material Balance, Wt%	100.7	104.3	102.4	106.7	102.3
Overall Material Balance, Wt%	100.0	103.8	102.1	107.8	103.3

Liquid Product Analysis:

	(FEED)				
Wt% Carbon	90.57	89.63	89.53	89.66	89.49
Wt% Hydrogen	6.38	9.81	9.66	9.65	9.6
Wt% Sulfur	.745	.021	.017	.018	.019
Wt% Nitrogen	.923	.17	.178	.204	.206
Wt% Oxygen	1.38	.369	.615	.468	.685
Specific Gravity (60/60)	1.0921	.9719	.9775	.976	.9769

Corrected Yields Based on Liquid Feed:

Carbon Monoxide, Wt%	0	0	0	0	0
Carbon Dioxide, Wt%	0	0	0	0	0
Ammonia, Wt%	.914	.904	.872	.869	.903
Hydrogen Sulfide, Wt%	.769	.774	.773	.772	.777
Water, Wt%	1.136	.856	1.024	.777	1.026
Hydrocarbon Gases (C1 - C4), Wt%	.408	.404	.417	.532	.555
Liquids (C5+), Wt%	100.7	100.8	100.7	100.7	100.4
Hydrogen Consumption, Wt% (analysis)	3.92	3.75	3.74	3.69	3.66
Hydrogen Consumption, Wt% (gas phase)	4.64	4.16	3.97	2.34	2.58

Corrected Conversions:

% Hydrodesulfurization	97.2	97.7	97.6	97.4	98.1
% Hydrodenitrogenation	81.4	80.6	77.7	77.5	80.5
% Hydrodeoxygenation	73.1	55.1	65.9	50.0	

Corrected Reaction Rates:

Sulfur Removal, GM/HR/GM	1.383	1.473	1.493	1.43	1.498
Nitrogen Removal, GM/HR/GM	1.435	1.504	1.473	1.409	1.523
Oxygen Removal, GM/HR/GM	1.926	1.538	1.867	1.359	1.868
Hydrogen Uptake, GM/HR/GM	6.681	6.794	6.843	6.484	6.597
Gas Make, GM/HR/GM (x E-3)	7.79	8.173	8.568	10.47	11.383

Table 1 (continued)
Run PDJ03, 5.0005 GMS Amocat 1A

Run Summary:

	6	7	8
Yield Period No.	6.0	6.0	6.0
Yield Period Length, HR	750	750	750
Average Temperature, F	399.1	398.8	399.0
Average Temperature, C	2010	2000	2010
Average Pressure, PSIG	10.17	10.2	10.25
Liquid Feed Rate, GM/HR	2.03	2.04	2.05
Weight Hourly Space Velocity	.492	.49	.488
Weight Hourly Space Time	8.17	8.17	8.17
Hydrogen Treat Rate, L(STP)/HR	4900	4880	4860
Hydrogen Treat Rate, SCF/BBL	1500	1500	1500
Stirrer Speed, rpm	4.58	4.78	4.82
Exit Gas Rate, L(STP)/HR	140.6	164.6	188.6
Cumulative Hours on Catalyst	288.1	337.5	386.9
Cumulative Wt. Oil/Wt. Catalyst	103.9	104.1	102.8
Liquid Material Balance, Wt%	103.2	103.4	102.2
Carbon Material Balance, Wt%	102.7	102.7	101.9
Overall Material Balance, Wt%			

Liquid Product Analysis:

	(FEED)			
Wt% Carbon	90.57	89.58	89.63	89.63
Wt% Hydrogen	6.38	9.59	9.51	9.57
Wt% Sulfur	.745	.013	.015	.015
Wt% Nitrogen	.923	.179	.187	.212
Wt% Oxygen	1.38	.638	.658	.573
Specific Gravity (60/60)	1.0921	.9768	.9773	.9782

Corrected Yields Based on Liquid Feed:

Carbon Monoxide, Wt%	0	0	0
Carbon Dioxide, Wt%	0	0	0
Ammonia, Wt%	.903	.893	.862
Hydrogen Sulfide, Wt%	.778	.776	.776
Water, Wt%	.831	.808	.905
Hydrocarbon Gases (C1 - C4), Wt%	.486	.477	.514
Liquids (C5+), Wt%	100.7	100.6	100.6
Hydrogen Consumption, Wt% (analysis)	3.68	3.59	3.66
Hydrogen Consumption, Wt% (gas phase)	4.14	4.26	3.94

Corrected Conversions:

% Hydrodesulfurization	98.2	98.0	98.0
% Hydrodenitrogenation	80.5	79.6	76.9
% Hydrodeoxygenation	53.5	52.0	58.2

Corrected Reaction Rates:

Sulfur Removal, GM/HR/GM	1.488	1.489	1.496
Nitrogen Removal, GM/HR/GM	1.509	1.498	1.454
Oxygen Removal, GM/HR/GM	1.5	1.465	1.647
Hydrogen Uptake, GM/HR/GM	6.66	6.508	6.658
Gas Make, GM/HR/GM (xE-3)	9.886	9.726	10.542

balances are suggestive of a small systematic error; however, additional data and more experience in operating the unit will be necessary in order to verify that a problem exists and to find the cause if indeed it does.

One very desirable feature of a backmix reactor is that reaction rates can be calculated directly. The reaction rates for hydrogen uptake (HYD), hydrodenitrogenation (HDN) and hydrodesulfurization (HDS) are plotted versus "catalyst service" (wt. oil processed/wt. catalyst) in Figure 3. From these curves it appears that steady-state is achieved by the first yield period and that the catalyst does not deactivate significantly during the run. The near superposition of the HDS and HDN rates is probably fortuitous. Hydrodesulfurization is nearly complete ($>95\%$), hence it is doubtful that any useful HDS kinetics information can be obtained at these operating conditions. See Figure 4. About 80 wt% of the nitrogen is removed. The oxygen content of the products was calculated by difference and consequently the % HDO and oxygen removal rates in Table 1 should not be viewed as quantitative.

Hydrogen consumption was calculated by two methods: 1) from analysis of the gas and liquid products (analysis), and 2) from the gas phase analysis for molecular hydrogen (gas phase). See Table 1. The analysis values are considered more reliable. Except for yield periods 4 and 5, which may be tainted as pointed out earlier, the gas phase values tend to be somewhat higher than the analysis values. Such discrepancies could arise from small hydrogen leaks. Still the two numbers are not grossly out of line and more work is needed to establish whether or not hydrogen consumption can be calculated from the gas phase analysis.

Figure 3. Reaction Rates for HYD, HDS and HDN, Run PDJ03.

Figure 4. HDS and HDN Conversions, Run PDJ03.

A major concern in any ebullated bed operation is the question of catalyst attrition. The used catalyst was THF extracted for 24 hours and vacuum dried at 100 - 110°C to constant weight. A portion of the THF extracted and dried catalyst was fired in a muffle furnace at 500°C for 16 hours (standard calcining procedure) and from the recorded weights, the percentage catalyst recovery relative to fresh calcined catalyst was calculated. This number is recorded in Table 2 along with values calculated from the earlier much shorter runs. Again there is no evidence of catalyst attrition. (The LOI is not recorded in Table 1 because it was felt that coke laydown may have been excessive due to the sudden loss of pressure while at reaction temperature.)

Additional CCLM Runs:

A short thermal run (no catalyst) was completed during the last quarter as was a much more extensive process variable study. Since no analytical results are yet available, the discussion of these runs will be deferred until the next report.

Table 2

Catalyst Recovery and Percent LOI

	<u>PDJ01</u>	<u>PDJ02</u>	<u>PDJ03</u>
Run Duration (hrs)	39	48	215
% Loss on Ignition	8.95	10.3	---
% Catalyst Recovery	99.87	99.88	100.5

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