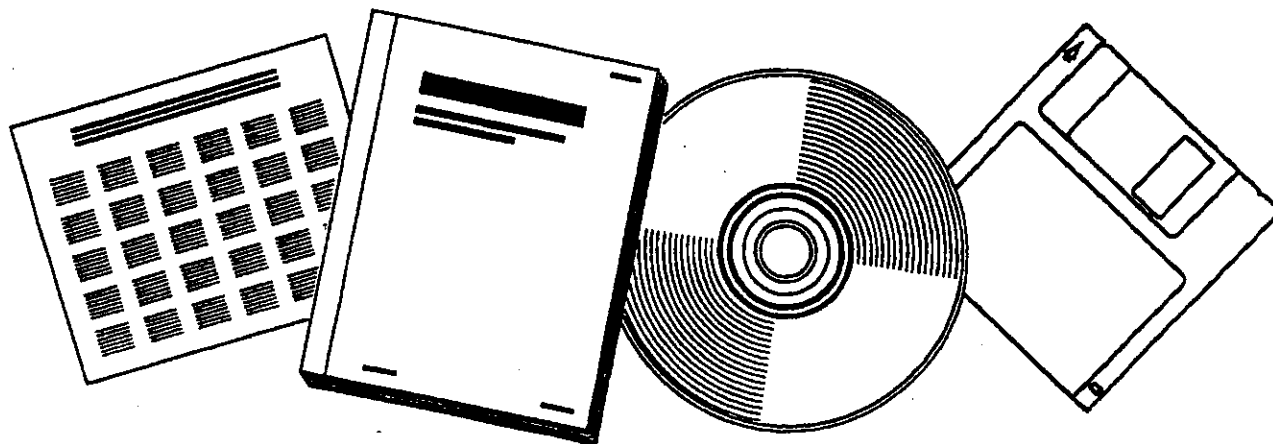**NTIS**

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IMPROVED FISCHER-TROPSCH SYNTHESIS CATALYSTS FOR INDIRECT COAL LIQUEFACTION: QUARTERLY TECHNICAL PROGRESS REPORT NO. 10 FOR THE PERIOD 1 JANUARY TO 31 MAY 1988

SRI INTERNATIONAL
MENLO PARK, CA

1988

DOE/PC/80016--T8

Quarterly Technical Progress Report No. 10
for the Period 1 January to 31 May 1988

IMPROVED FISCHER-TROPSCH SYNTHESIS CATALYSTS FOR INDIRECT COAL LIQUEFACTION

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SUMMARY

The synthesis of aromatics was performed on several combinations of Fischer-Tropsch (FT) and sodium Y-zeolite catalysts in a fixed-bed reactor with an H_2/CO ratio of 0.5, 2.0-MPa pressure, and a temperature range of 548 to 700 K. Medium-level sulfur-treated fused iron and sulfur-treated alumina-supported ruthenium were used as the Fischer-Tropsch synthesis catalysts and compared with results using clean fused iron and clean ruthenium catalysts. The mixed catalysts initially provided high yields of light oxygenates and aromatics with low yields of olefins but deactivated rapidly, probably due to carbon deposition, especially at higher temperatures. The catalyst reactivity could be prolonged by using a higher zeolite/FT catalyst ratio and by using zeolites with higher sodium weight loading.

These results compare favorably with prior similar studies performed under less severe coking conditions. Additional work with high-silica shape-selective zeolite components to extend the catalyst active life is recommended at high syngas conversion using sulfur-treated iron catalysts.

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INTRODUCTION

Single-stage direct conversion of synthesis gas into aromatic hydrocarbons is a demonstrated catalytic process. Combinations of acidic synthetic zeolites, such as Mobil's ZSM-5 and FT synthesis catalysts, have been shown by Chang et al.[1,2], Seitzer,[3] and Rao et al.[4] to produce benzene, toluene, and mixed xylenes from synthesis gas with high selectivity. Combinations of catalysts selective for methanol synthesis and ZSM-5 or other zeolites have also been shown by Shamsi et al.,[5] Bruce et al.,[6] and Varma et al,[7,8] to produce BTX with high selectivity. The zeolite may synergistically convert the unstable intermediate synthesis products, olefins or alcohols, into the more thermodynamicaly stable aromatics. However, the advantage of single-stage reaction is generally offset by the disadvantage that the operating conditions of these sequential reactions are not optimal.[9-11] As a consequence, Mobil has developed the methanol-to-gasoline (MTG) process with ZSM-5 to convert synthesis gas into gasoline following conventional methanol synthesis, a commercially established technology.

Single-stage aromatics synthesis has two principal disadvantages: (1) compromised operating conditions that lead to less than optimal yields and (2) the deactivation of the catalytic active components by carbon deposition (coking). FT synthesis or methanol synthesis is thermodynamically favored at low temperature and high pressure, whereas conversion of olefins or alcohols to aromatics is favored at high temperature and low pressure. Low temperature operation (500 K) slows conversion into aromatics, whereas high temperature operation (700 K) tends to produce too much light alkane, especially methane and promotes rapid deactivation due to carbon deposition on the catalyst. Thus, the synergistic potential of dual-function catalysts to produce high selectivity and high conversion has not been realized, and two-stage processing is currently a more attractive technology.

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Direct aromatic hydrocarbon synthesis over a dual-function catalyst with unusually low concentrations of hydrogen in the reactant gas has the potential advantages of high aromatic yields, stoichiometrically limited methane yield, relatively dry product gas, and (of course) nearly complete hydrogen consumption. The principal difficulty in processing low hydrogen synthesis gas is the need to suppress the greater tendency for carbon deposition on the catalyst and subsequent catalyst deactivation.

We have investigated several combinations of zeolites and the coking-resistant sulfur-treated fused iron catalysts for FTS performance and aromatic hydrocarbon production in a fixed-bed reactor with low hydrogen syn gas. The goals of this work were to explore process conditions that give high yields of aromatics and to determine the rate and nature of deactivating coke formation.

EXPERIMENTAL RESULTS

In our preceding studies with sulfur-treated fused iron catalysts, we found that partially sulfur-covered iron surfaces produced less saturated light alkanes than untreated catalysts and exhibited no observable coking tendency. The medium-level sulfur-treated iron catalysts prepared as described previously were mixed with zeolite and tested at 2 MPa for their ability to produce aromatics in syn gas with $H_2/CO = 0.5$. In addition, a new sulfur-treated catalyst Ru/Al_2O_3 was prepared for this study using the same sulfur treatment procedure.

The alumina-supported ruthenium FTS catalyst was treated with H_2S until sulfur was chemisorbed to a coverage of about one-half saturation. Following a more severe passivation procedure (exposure to 99.5% CO at 523 K after addition of 10.4% C_2H_4/He), the rate of sulfur adsorption at 425 K was slowed to about monolayers per hour in a recirculating stream of 10 ppm H_2S in 100-kPa H_2. After removal of the carbon overlayer in 1-atm H_2 at 773 K, the catalyst was removed from the sulfur treatment apparatus, reduced, and tested for aromatics synthesis performance in the fixed-bed FTS reactor system.

We examined the aromatics synthesis performance of the medium-level sulfur-treated fused iron catalyst, the medium-level sulfur-treated alumina-supported ruthenium, the clean alumina-supproted ruthenium, and the fused iron standard catalyst, all in combination with Union Carbide Na-Y zeolites (with sodium content 0.2 wt% [LZY-52], 2.0 wt% [LZY-62], and 10 wt% [LZY-82]). The results are given in Table 1. Tests were performed in a fixed-bed reactor at 2 MPa, H_2/CO ratio = 0.5, and 548 to 700 K. The catalyst bed was a physical admixture of the FT and zeolite catalyst powders (10/14 mesh) of various weight ratios (zeolite/FT catalyst ratio = 4 or 10) maintained at a constant temperature. Typically, the CO conversion was about 20% at a gas hourly space velocity (GHSV) of 1×10^4 to 2×10^4 h^{-1}. GHSV is defined as the hourly flow rate (NTP) of CO + H_2 per unit volume of the FT catalyst component.

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Table 1

SYNTHESIS OF AROMATICS AND OXYGENATES BY MIXTURES

SULFUR-TREATED FUSED IRON AND ZEOLITE CATALYSTS

Catalyst	Medium-Level Sulfur Treated Fused Iron	Medium-Level Sulfur-Treated Fused Iron + LZY-82 Zeolite (1:4 by wt)	Medium-Level Sulfur-Treated Fused Iron + LZY-52 Zeolite (1:4 by wt)	Medium-Level Sulfur-Treated Fused Iron + LZY-62 Zeolite (1:10 by wt)	Medium-Level Sulfur-Treated Fused Iron + LZY-52 Zeolite (1:10 by wt)			
Temperature (K)	573	573	573	573	573	650	650	700
Pressure (MPa)	2	2	2	2	2	2	2	2
H_2/CO Ratio	1	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Run Duration (h)	24	2	2	2	2	1.5	23.5	1
Production Rate[a] (nmol/g/s)								
C_1	53.86	262.28	326.62	162.09	165.78	153.32	222.39	193.67
C_2	43.07	63.66	183.18	33.27	62.66	58.13	67.63	59.87
C_3	34.71	106.90	166.96	39.69	31.40	52.06	72.97	56.98
C_4	17.30	53.11	119.34	20.40	15.49	26.98	47.47	25.26
Oxygenates	2.17	451.00	173.49	190.19	176.47	272.47	14.34	205.10
Aromatics	0.03	0.00	59.67	11.21	13.67	34.24	4.72	20.55
TOTAL	401.16	1743.20	2901.80	870.10	930.20	1662.60	1080.10	1199.60
Chain Growth Factor[b]	0.52	0.34	0.71	0.45	0.61	0.56	0.50	0.40
1-Butene to Butane Ratio[c]	0.85	0.00	0.76	0.00	0.07	0.12	0.70	0.06
Methane Selectivity[d]	14.76	11.54	11.53	15.60	15.10	8.58	22.00	14.20
Oxygenate Selectivity	1.24	57.00	15.10	51.71	39.90	38.60	3.61	38.20
Aromatic Selectivity	0.52	0.00	11.90	3.61	6.30	16.80	2.51	8.08

[a] GHSV = 600 h⁻¹; Product rate for each carbon number includes n-paraffins and α- and β-olefins; total product rate is on a carbon-atom basis.

[b] Average chain growth parameter (α) for C_{3+} hydrocarbons.

[c] Average olefin to paraffin ratio for C_2 to C_6 hydrocarbons.

[d] C_1 rate/(total rate) x 100 %.

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After 2 hours at 573 K, the methane yields of the sulfur-treated fused iron only and in Na-Y zeolite combinations were 11 and 15 wt%. The oxygenate (methanol and dimethylether) and aromatic (benzene, toluene, ethylbenzene, and xylenes) yields of the sulfur-treated fused iron, Na-Y zeolite combinations were much greater than for fused iron alone. The amount of oxygenates initially produced (after 2 hours) depended heavily on the sodium weight loading of the zeolite of the mixed catalyst (see Table 1). The chain growth parameter, α, decreased substantially from 0.71 to 0.34 with increased oxygenate and aromatic hydrocarbon selectivity. The methane yield remained low and decreased slightly for catalysts with the smallest zeolite component.

However, the combinations of fused iron and zeolite catalysts were prone to deactivation by carbon deposition in hydrogen-deficient synthesis gas. After 24 hours of synthesis reaction, the product distribution typically resembled that of the sulfur-treated fused iron catalyst alone (see Figure 1). The decreased oxygenate and aromatics yields were nearly matched by increased olefin yield, suggesting that the zeolite component of the mixed catalyst was fouled and deactivated, probably by carbon deposition. The deactivation was most pronounced for the zeolite with low sodium weight loading. However, the catalysts could be regenerated by reaction of the deposited carbon with pure hydrogen at 773 K and 100 kPa for 2 hours. To prolong the useful life of the catalyst, especially at higher temperatures, we used a larger amount (10:1 versus 4:1) of a less acidic (higher sodium content, LZY-52) zeolite in combination with sulfur-treated iron catalyst. This zeolite combination also showed evidence for deactivation in the form of decreased oxygenate and aromatic yields at 650 K (Table 1).

In comparing the selectivity of these mixed catalysts, we found that the one with low sodium (LZY-82) produced predominantly oxygenates, with high conversion of the light olefins. The mixed catalyst with high sodium (LZY-52) produced a mixture of oxygenates and aromatics of roughly equal proportion with a correspondingly lower conversion of the light olefins (see Figure 2). The mixed catalyst (with LZY-62) had a product distribution similar to that of the LZY-52 mixed catalyst.
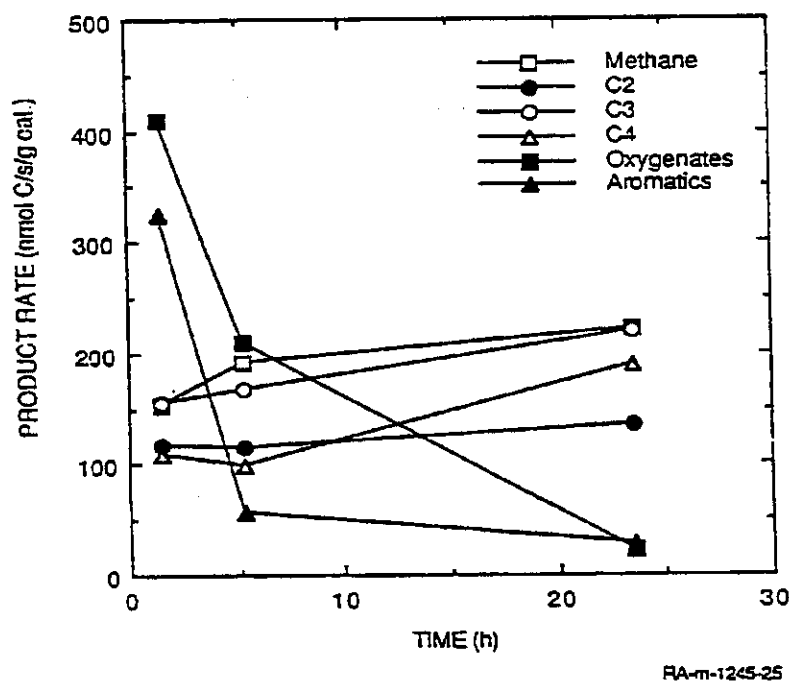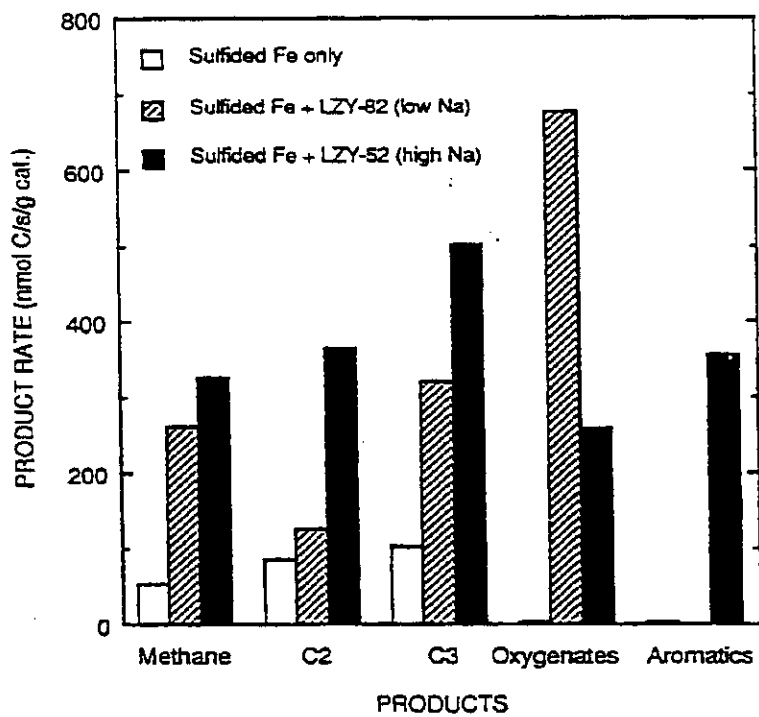
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RA-m-1245-25

Figure 1.   Aromatic synthesis at 573 K, 2 MPa, H_2/CO ratio = 0.5 on
medium-level sulfur-treated fused iron catalyst and LZY-52
zeolite (1:10 wt ratio).

Figure 2. Aromatic synthesis at 2 MPa, 573 K, H_2/CO ratio = 0.5, on mixed medium-level sulfur-treated fused iron and Na-Y zeolite catalyst.
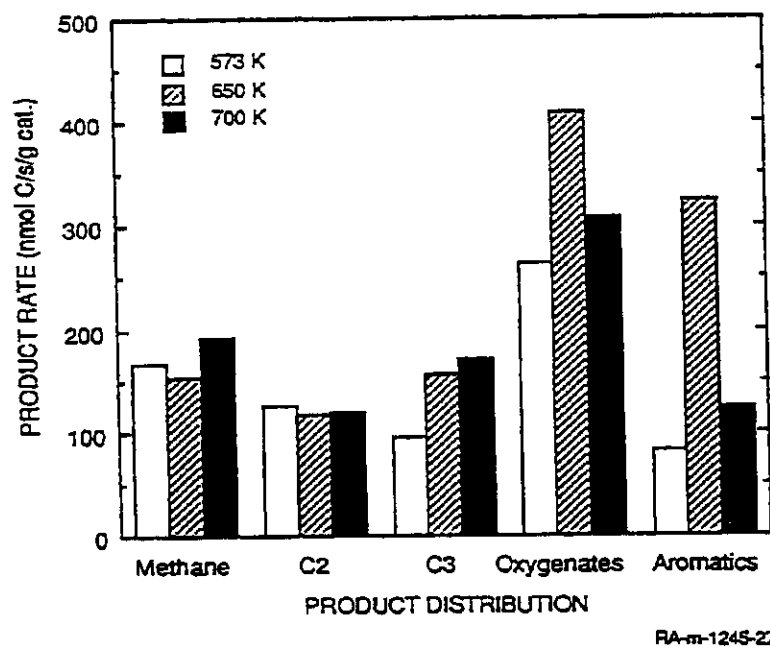
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Figure 3.   Effect of temperature on the initial product distribution for the
(1:10) medium-level sulfur -treated fused iron and high
sodium zeolite composite catalyst.

The activity of the sulfur-treated alumina-supported ruthenium/Na-Y zeolite catalyst was a factor of ten lower than that of the sulfur-treated fused iron/Na-Y zeolite catalyst at 573 K. However, the oxygenates and aromatics selectivities (28 wt% and 17 wt%, respectively) of the ruthenium/Na-Y zeolite mixed catalysts were roughly the same as the fused-iron mixed catalyst. The lower activity of the ruthenium mixed catalyst (per unit weight FT catalyst) was primarily due to its much lower metal weight loading (2.4 wt% Ru) compared with the bulk fused iron mixed catalyst. The sulfur-treated ruthenium mixed catalyst showed 50% decreased methane and a factor of two increased oxygenates and aromatics yields at both 573 and 598 K when compared with the clean ruthenium mixed catalyst (see Table 2).

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Table 2

SYNTHESIS OF AROMATICS AND OXYGENATES BY MIXTURES
OF SULFUR-TREATED RUTHENIUM AND ZEOLITE CATALYSTS

Catalyst	Clean 2.4 wt% Ru/Al_2O_3 + LZY-52 Zeolite (1 to 10 wt ratio)		Medium-level Sulfur-treated 2.4 wt% Ru/Al_2O_3 + LZY-52 Zeolite (1 to 10 wt ratio)	
Temperature (K)	598	573	598	573
Pressure (MPa)	2	2	2	2
H_2/CO ratio	0.5	0.5	0.5	0.5
Duration (h)	2	2	2	2
Product rate[a] (nmol/s/g cat)				
C_1	22.96	5.20	23.44	10.32
C_2	2.37	0.55	2.55	1.14
C_3	1.72	0.89	2.33	1.56
C_4	1.11	0.84	1.56	1.42
Oxygenates	1.83	1.31	4.63	7.27
Aromatics	0.20	0.54	0.89	2.03
TOTAL				
Chain Growth Factor[b]	0.48	0.55	0.50	0.66
1-Butenes to Butane Ratio[c]	0.44	0.73	0.52	0.62
Methane Selectivity[d]	50.90	26.30	37.90	16.10
Oxygenates Selectivity	9.70	15.60	17.80	27.50
Aromatics Selectivity	2.10	13.50	7.64	16.80

[a]GHSV = 600 h^{-1}; Product rate for each carbon number includes n-paraffins and α- and β-olefins; total product rate is on a carbon-atom basis.

[b]Average chain growth parameter (α) for C_{3+} hydrocarbons.

[c]Average olefin to paraffin ratio for C_2 to C_6 hydrocarbons.

[d]C_1 rate/(total rate) x 100%.

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DISCUSSION

The synthesis of aromatic hydrocarbons was performed under differential reactor condition because of the constraints of maximum catalyst bed volume and minimum controllable syn gas flow rate at elevated pressure. As a result, the overall conversion of the syn gas was limited to 20% and was relatively insensitive to temperature (see Table 1). The aromatics yield increased threefold with a corresponding decrease in methane yield by increasing the reactor temperature from 573 K to 650 K (see Figure 3). However, additional increase in reactor temperature to 700 K resulted in more rapid deactivation of the zeolite catalyst without additional enhancement in aromatics selectivity or syn gas conversion.

The yield of aromatics in the synthesis product using the mixed sulfur-treated iron and zeolite catalyst may have been limited by the low conversion of the synthesis gas. The presence of unreacted hydrogen and product water vapor perhaps inhibited the dehydrocyclization reaction and favored the formation of dimethylether and methanol, which can be considered intermediates for aromatic hydrocarbons on zeolite catalysts such as HZSM-5.[9,10] The acidic properties of the low-sodium zeolite enhanced the formation of oxygenate and aromatic hydrocarbon, but also enhanced cracking and led to more rapid deactivation of the catalyst.

Since the strong acidic sites in the zeolite are responsible for the formation of aromatics by the dehydrocyclization of the C_6 olefins, the observed decrease in oxygenates and aromatics selectivity with time can be attributed to the progressive deactivation of these sites by coking. The deactivation of the zeolitic component of the catalyst resulted in loss of isomerization and dehydrocyclization activity to formed aromatics and isoparaffins. The use of a higher weight ratio of zeolite to FT catalyst in the mixed bed mode definitely prolonged the activity and increased oxygenates and aromatics selectivity compared with the catalyst with smaller amount of zeolite.

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The consumption of light olefins, which are essential building blocks for aromatics, to form oxygenates effectively decreased the selectivity of aromatics in the product. Also, it has been postulated[9] that the formation of aromatics is the rate-limiting step of the overall conversion of methanol to aromatics on HZSM-5. The completing cracking and hydrogenolsis reactions of the olefins apparentaly led to low aromatics yield and to carbon deposition on the zeolite of the mixed catalyst.

REFERENCES

1. C. D. Chang, W. H. Lang, and A. J. Silvestry, J. Catalysis <u>56</u>, 268 (1979).

2. C. D. Chang and W. H. Lang, Mobil Oil, U.S. Patent 4180516 (1979).

3. W. H. Seitzer, Suntech, U.S. Patent 4139550 (1979).

4. V. U.S. Rao, R. J. Gormley, H. W. Pennline, L. C. Schneider, and R. Obermyer, ACS Division of Fuel Chem. Preprints <u>25</u>(2), 119 (1979).

5. A. Shamsi, U. Rao, R. J. Gormley, R. T. Obermyer, R. R. Schehl, and J. M. Stencel, Ind. Eng. Chem. Prod. Res. Dev. <u>23</u>, 513 (1984).

6. L. Bruce, G. T. Hope, and J. F. Mathews, Appli. Catal. <u>9</u>, 351 (1984).

7. R. L. Varma, K. Jothimurugesan, N. N. Bakhshi, J. F. Mathews, and S. H. Ng, Can. J. Chem. Eng. <u>64</u>, 141 (1986).

8. R. L. Varma, D.-C. Liu, J. F. Mathews, and N. N. Bakhshi, Can. J. Chem. Eng. <u>63</u>, 72 (1985).

9. H. W. Pennline, V.U.S. Rao, R. J. Gormley, and R. B. Schehl, ACS Div. Fuel Chem. Preprints <u>28</u>, 164 (1983).

10. T. J. Huang and W. O. Haag, ACS Symposium Series <u>152</u>, 307 (1981).

11. R. L. Varma, N. N. Bakhshi, J. F. Mathews, and S. H. Ng, Ind. Eng. Chem. Res. <u>26</u>, 183 (1987).