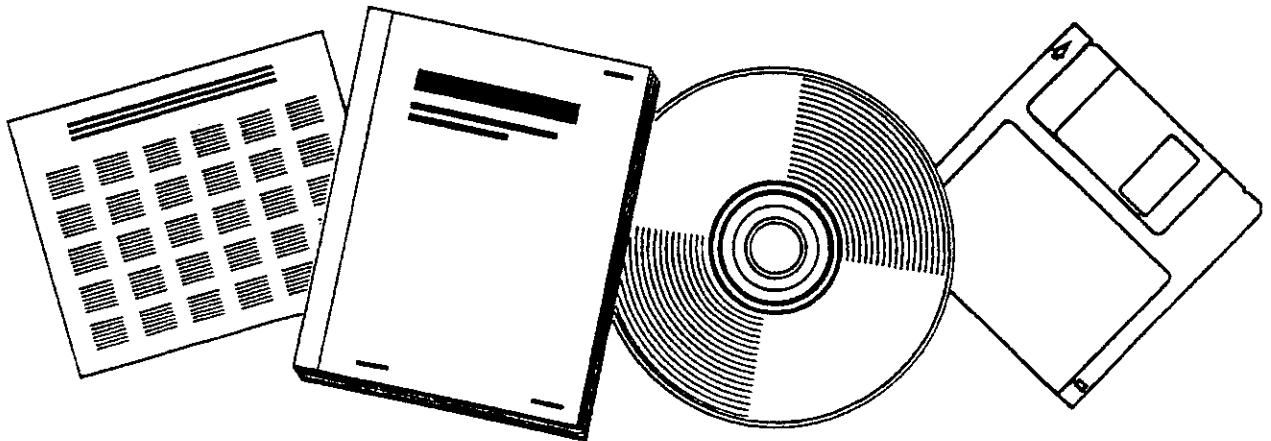DE82008199   40771-3

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FISCHER-TROPSCH SYNTHESIS IN SLURRY-REACTOR SYSTEMS. QUARTERLY REPORT, NOVEMBER 1, 1981 TO JANUARY 31, 1982

MASSACHUSETTS INST. OF TECH., CAMBRIDGE

1982

Fischer-Tropsch Synthesis in Slurry-Reactor Systems

Quarterly Report for Period

November 1, 1981 to January 31, 1982

Department of Chemical Engineering

and

Energy Laboratory

Massachusetts Institute of Technology

Cambridge, Massachusetts

MASTER

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I. SUMMARY

A detailed study of mass transfer effects with a reduced fused magnetite catalyst has now been completed and is summarized in an appended paper, "Mass Transfer and Product Selectivity in a Mechanically-Stirred Fischer-Tropsch Slurry Reactor," by Charles N. Satterfield and George A. Huff, Jr.

Analysis of our heavier hydrocarbon products indicates that they yield a value of $\alpha = 0.93$ on a Flory plot, considerably higher than the values of α of about 0.7 found with lighter products. Iron catalysts may exhibit two kinds of sites with considerably different kinetic behaviour.

At the request of Drs. Sapienza and Slegeir of the Brookhaven National Laboratory, we ran a sample of their SOSS catalyst in our reactor facility at 100 psig. Activity was low, but this may have been because this particular catalyst is possibly better suited for higher pressures.

II. DETAILED RESULTS

A. Mass Transfer and Product Selectivity

A detailed study of mass-transfer effects with a reduced fused magnetite catalyst has now been completed. Studies were made at 232, 248 and 263°C at 790 kPa and with a variety of stirring speeds. These results showed that a substantial gas-to-liquid mass transfer resistance can be encountered, which causes the paraffin to olefin ratio of the hydrocarbon products to decrease. Under intrinsic kinetic conditions this ratio increases with hydrogen concentration in the liquid but is independent of carbon monoxide concentration. Hence with significant mass-transfer, this ratio is governed by the resistance to H_2 transfer rather than by the effective H_2/CO ratio in the liquid.

The work is summarized in a paper attached to this report entitled, "Mass Transfer and Product Selectivity in a Mechanically-Stirred Fischer-Tropsch Slurry Reactor," by Charles N. Satterfield and George A. Huff, Jr. It will be presented at the 7th International Symposium on Chemical Reaction Engineering to be held in Boston in October 1982.

In the future some studies will be made of mass transfer effects on cobalt and perhpas ruthenium catalysts. Secondary reactions appear to be much more prominent on cobalt than on iron and thus the apparent selectivity with cobalt may be mroe greatly affected by mass transfer.

B. Analysis of Slurry Wax

As projected last quarter, a sample of our slurry wax was analyzed by an outside laboratory. A Flory plot of the results in Figure 1 shows a straight line for the $C_{30}+$ hydrocarbons.

The value of α, 0.93, for this fraction of the product distribution is substantially higher than that obtained from the C_1 to C_{15} fraction that is volatilized out of the reactor. This and other evidence suggests that two α values are necessary to describe adequately the true product distribution from an iron catalyst. We are currently modeling some of our results in terms of a two-site model, each with a different α value.

C. Potassium Content

The potassium content of an iron catalyst is the most important factor affecting the product distribution expressed as an α value. An outside analysis is currently being conducted to determine the amount of potassium present in our particular catalyst batch, since the catalyst manufacturer reports only a range for the potassium content.

D. Studies with Added Ethylene

The proposed studies with spiked ethylene feeds have been completed. Analysis of the trapped liquid samples from the run are not available yet but should be completed during the next quarter. A short test is scheduled for the coming quarter using a feed spiked with butylene to compare its behaviour to that observed for ethylene.

E. SOSS Catalyst

We were requested by Rich Sapienza and Bill Slegeir of the Brookhaven National Lab to conduct a run with the SOSS catalyst in our continuous reactor system. This was done in January 1982 in the presence of Sapienza and Slegeir. The catalyst, a Pt/Co alloy, is reported to have very high activity, but had previously only been run in a batch reactor and only for a few hours duration.

The run, utilizing 50 g of their catalyst, was forced to end after 66 hours of operation at 248°C due to plugging problems. The small amount of data taken (light gas analysis and conversion data) indicated that the catalyst did not have significant activity at 100 psig. At the conclusion of the run the catalyst was recovered (96% yield) and returned to Brookhaven for surface and bulk composition analysis. Slegeir commented that this particular SOSS catalyst was more suitable for higher pressures because of the relatively low surface area of the support.

F. Publications

The progress report for the period ending July 31, 1981 contained preprints of four papers submitted for publication. Two of these have now been published, as follows: "Effect of Carbon Formation on Liquid Viscosity and Performance of Fischer-Tropsch Bubble-Column Reactors," by Charles N. Satterfield, George A. Huff, Jr., and Harvey G. Stenger, I&EC Proc. Des. Dev., 1981, 20, 666, and "Carbon Number Distribution of Fischer-Tropsch Products Formed on an Iron Catalyst in a Slurry Reactor," by Charles N. Satterfield and George A. Huff, Jr., J. Cat., 1982, 73, 187.

The other two have been formally accepted and should appear in the near future.

The quarterly for August - October 1981 contained a copy of a paper prepared for publication entitled, "A Stirred Autoclave Apparatus for Study of the Fischer-Trospch Synthesis in a Slurry-Bed I. Reactor and Trapping Procedures," by George A. Huff, Jr., and Charles N. Satterfield. The second part of this paper, on detailed analytical procedures, is being written and a copy should be available during the next quarter. Some of the

analytical work is being done in cooperation with Dr. Martin Wolf

of the Cambridge Analytical Associates who are providing GC/MS

analyses on representative products.

III. FUTURE WORK

Fused Iron Intrinsic Kinetic Results:

The doctoral thesis of George Huff will be completed in March

and will address the detailed kinetic results on the reduced

fused magnetite catalyst including both activity and selectivity

effects. A summary of this aspect of the work will be presented

in the next quarterly report.

Analytical:

Although our reactor-trapping system has the capability to

remove small liquid samples from the slurry, this option has not

been utilized previously. Obtaining these slurry samples during

a synthesis run would allow (1) analysis for high molecular

weight products, (2) determination of free carbon and (3) catalyst

characterization.

The analysis of heavy molecular weight products that are

retained in the reactor is of primary interest for several

reasons. Runs conducted with a cobalt catalyst must be made

at lower temperatures (typically 175 to 225°C) than the fused

iron catalyst (240 to 270°C) to prevent catalyst deactivation.

These lower temperatrues will result in a larger fraction of

the products being retained in the reactor. Sampling of the

slurry will also permit an accurate accounting of all the products

formed, allowing a test of the Flory distribution for high carbon

number products ($C_{20}+$).

Analysis of these samples using our capillary column gas

chromatograph is not advisable, since high molecular weight

hydrocarbons are retained on the column, thus shortening the column life and varying its transfer properties. However, a liquid chromatograph is available for continuous use by our group and is perhaps the best method for analyzing these slurry samples. During the next quarter the setup and testing of the liquid chromatograph unit will begin.

Other Catalysts:

It is planned to make runs of moderate length with other iron catalysts using extensive data based on reduced fused magnetite as a basis for comparison. When these are concluded we plan then to consider certain cobalt catalysts.

Catalyst Reduction:

It is known that the rate of reduction of the fused magnetite ammonia synthesis catalyst can substantially affect its intrinsic activity, presumably associated with catalyst sintering. At typical reduction temperatures (380-450°C) sintering is due to an increased mobility of the iron atoms upon loss of neighboring oxygen atoms. The more rapid the removal of oxygen through the production of water, the greater the rate of sintering. A moderate variation in catalyst activity on a per gram basis from run to run indicates that our reduction rates may be causing some amount of sintering. A short run with the fused iron catalyst reduced slowly as determined by the exiting water concentration is planned to test this hypothesis.

Slurry Wax Analysis
Run Fe-9 - 8/4/81
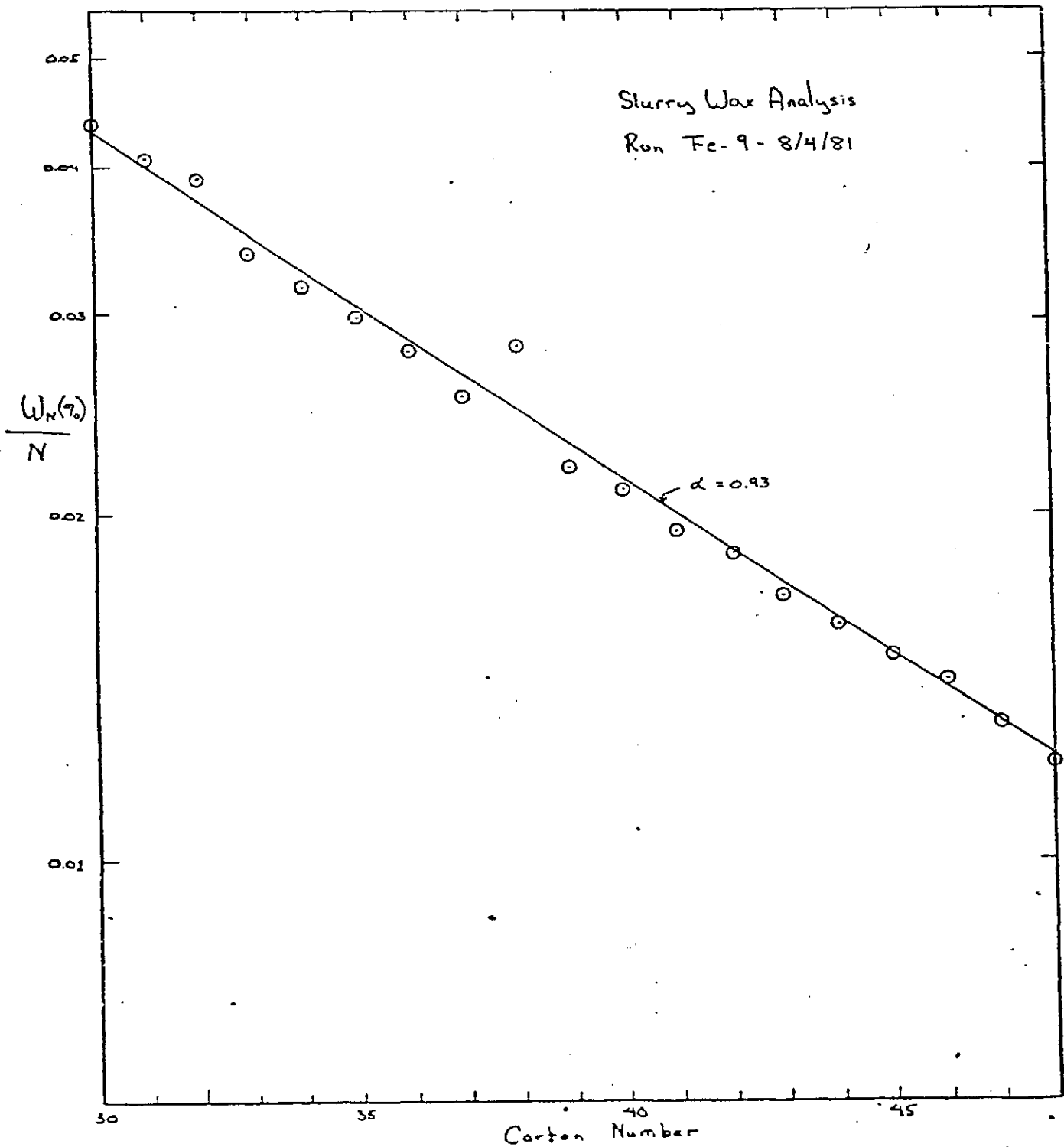
$\alpha = 0.93$

$\frac{W_N(\%)}{N}$

Carbon Number

Mass Transfer and Product Selectivity in a Mechanically-Stirred Fischer-Tropsch Slurry Reactor

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Abstract

With a fused iron catalyst a substantial gas-to-liquid mass transfer resistance can be encountered, which causes the paraffin to olefin ratio of the hydrocarbon products to decrease. Under intrinsic kinetic conditions this ratio is approximately proportional to the half-power of hydrogen concentration in the liquid but is independent of carbon monoxide concentration. Hence with significant mass-transfer, this ratio is governed by the resistance to H_2 transfer rather than by the effective H_2/CO ratio in the liquid.

* * *

With a finely divided solid catalyst as typically used in the Fischer-Tropsch synthesis in slurry reactors it is generally agreed that the major mass-transfer resistance, if it occurs, does so at the gas-liquid interface. There are considerable disagreements about the magnitude of this resistance, that stem from uncertainties about certain physical parameters, notably interfacial area, but also the solubility and mass transfer coefficients for H_2 and CO that apply to this system. However when this resistance is significant, the concentrations of H_2 and CO in the liquid in contact with the solid catalyst become less than they would be otherwise, which not only reduces the observed rate of reaction, but can also affect the product selectivity and the rate of formation of free carbon.

Experimental: Studies were carried out in a one-liter, mechanically-stirred autoclave operated in a semi-continuous fashion in that the catalyst and liquid carrier (normal-octacosane) remain in the reactor whereas synthesis gas is sparged to the reactor and volatile products removed overhead. The phases are well mixed, which simplifies interpretation of experimental results. Moreover, the degree of mass transport can be controlled by varying the degree of agitation, since gas-liquid interfacial area increases with power input. The autoclave has a diameter of 7.6 cm with two baffle bars (0.75-cm wide) that are spaced 180° apart. It is agitated with a 5.08-cm diameter propeller (3 blades at a 45° pitch) set above a six flat-bladed disk (each 1.27-cm square) turbine impeller 5.08 cm in diameter. The impeller is 3.5 cm above the wide-conical bottom of the reactor. Gas is fed through a 0.32-cm i.d. hole in the center of the bottom. Either a hollow or solid shaft stirrer can be employed. The hollow shaft agitator increases gas recirculation from top to bottom and the fact that we found no difference in our results between the two types is additional evidence that the system behaves as a CSTR. Further details of the apparatus and analytical procedures are available elsewhere (Huff and Satterfield, 1981; Huff et al., 1982).

The catalyst was a fused iron, type C-73, from United Catalysts, Inc. and normally employed for ammonia synthesis. It contained 2-3% Al_2O_3, 0.5-0.8% K_2O, 0.7-1.2% CaO and < 0.4% SiO_2, on an unreduced basis. It was crushed to a particle size smaller than 53 microns (270 A.S.T.M. sieve) and pre-reduced in a separate tubular reactor with hydrogen at 400°C, atmospheric pressure and space velocity of 5000 cm^3 gas (S.T.P.)/cm^3 catalyst-hour. It was then slurried with 450 g of octacosane (> 99% purity) to produce a 15 weight-percent suspension, based on unreduced catalyst weight. Cold studies in a transparent mock-up indicated that this finely divided catalyst did not settle on the reactor bottom at stirring speeds above 200 RPM. Two runs are reported on here, each

of which encompassed several hundred hours during which a variety of conditions were studied. A separate catalyst batch was used for each of the two.

Catalytic Activity: Figure 1 depicts the effect of changing the stirring speed on the conversion of hydrogen plus carbon monoxide at each of three temperatures. Two distinct regions appear in the curves with a transitional zone at about 400 RPM. In all cases, conversion becomes independent of agitation and strongly dependent on temperature at the higher degrees of agitation. As expected from theory, a faster stirring speed is required to move out of the gas-liquid controlling region at 263°C than 232°C.

Intrinsic Kinetics: Detailed information on the intrinsic kinetic expression for this catalyst is available elsewhere (Satterfield and Huff, 1982-a). The water-gas-shift reaction proceeds essentially to equilibrium (and hence completion) under our conditions, and based on the observed product composition, the stoichiometry for the reaction becomes:

$$6 \ CO + 7/2 \ H_2 \rightarrow C_3H_7 + 3 \ CO_2. \tag{1}$$
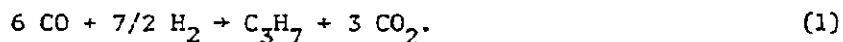
The intrinsic data were well correlated by a Langmuir-Hinshelwood type of expression which for the conditions here, reduces to an expression zero order in CO and first order in H_2:

$$-R_{H_2+CO} = -19/7 \ R_{H_2} = -19/12 \ R_{CO} = k \ C_{H,L}. \tag{2}$$

Although water vapor exerts an inhibiting effect on the rate (Dry, 1976), its concentration here was so low, because of the low H_2/CO ratios used and the occurrence of the water-gas-shift reaction, that its influence can be ignored. Equation (2) can be re-written in terms of partial pressure of H_2 by applying Henry's law, $P_H = m_H C_{L,L}$:

$$-R_{H_2+CO} = (k/m_H)P_H. \tag{3}$$

In the analyses that follow, it is further assumed that the hydrogen to carbon monoxide usage ratio is independent of conversion and given by a value of 7/12.

Mass Transfer: Since the intrinsic rate is independent of carbon monoxide concentration, we need consider only the mass transfer of hydrogen across the gas-liquid interface from the standpoint of activity. However both reactant material balances need to be considered in the more general case since the true concentration of carbon monoxide at the catalyst surface may alter selectivity:

$$-R_{H_2} = \frac{k_{L,H} \ a}{(1 - \varepsilon_G)} \ (C^*_{H,L} - C_{H,L}) \tag{4}$$

and

$$-R_{CO} = \frac{k_{L,C} \ a}{(1 - \varepsilon_G)} \ (C^*_{C,L} - C_{C,L}). \tag{5}$$

The concentrations of hydrogen and carbon monoxide in the liquid are given upon rearrangement of equations (4) and (5), respectively, as:

$$C_{H,L} = \frac{P_H}{m_H} - \frac{7(1-\varepsilon_G)(-R_{H_2+CO})}{19 \ k_{L,H} \ a} \tag{6}$$

and

$$C_{C,L} = \frac{P_C}{m_C} - \frac{12(1-\varepsilon_G)(-R_{H_2+CO})}{19 \ k_{L,C} \ a}. \tag{7}$$

Equations (6) and (4) can be combined to eliminate $C_{H,L}$ as:

$$\underbrace{\frac{P_H}{m_H (-R_{H_2+CO})} = \underbrace{\frac{7(1-\varepsilon_G)}{19\, k_{L,H}\, a}}_{\text{mass transfer}} + \underbrace{\frac{1}{k}}_{\text{intrinsic}} = \underbrace{\frac{1}{k_o}}_{\text{observed}}}_{} , \qquad (8)$$

where an overall apparent rate constant k_o is defined by:

$$-R_{H_2+CO} = (k_o/m_H)P_H \quad . \qquad (9)$$

From equation (8) values of the mass transfer component $\chi = k_{L,H}\, a/(1-\varepsilon_G)$ can be estimated from measured values of $-R_{H_2+CO}$ under mass transfer-limited conditions by using values of k determined from intrinsic kinetic studies. The actual concentrations of hydrogen and carbon monoxide in the liquid can then be calculated from equations (4) and (5), respectively. Values of k_o, the apparent rate constant, calculated by equation (9) for the same experimental runs depicted in Fig. 1, divided by hydrogen solubility, are plotted on a logarithmic scale against reciprocal temperature in Fig. 2. The linear correlation at the highest stirring speed with an activation energy of 100 kJ/mol is further indication that these data are intrinsic and unaffected by mass transfer. The data at constant, lower, stirring speeds exhibit the classical shapes expected by a reaction that becomes increasingly controlled by mass transfer.

The dashed lines in Fig. 2 are theoretical curves predicted by equation (8), based on the average mass transfer term χ back-calculated at each temperature and same stirring speed. Physical transport appears to be relatively independent of temperature and conversion even though it increases markedly with stirring speed. Increased gas contraction (and hence lower superficial velocity) associated with the higher conversions at higher temperatures affects both gas hold-up ε_G and interfacial area a in gas-liquid systems with mechanical agitation (Calderbank, 1958). However, the data of Westerterp et al. (1963) indicate that $a/(1-\varepsilon_G)$ is insensitive to gas-flow rate.

Values of χ are plotted in Fig. 3 for two runs, one using a solid-shaft stirrer and a second using a hollow-shaft agitator. Within the scatter of the data, there appears to be no difference between the two runs, indicating that the contents are indeed well mixed, even at lower stirring speeds. The component χ varies with stirring speed to the 4 ± 1 power in our combined propeller/impeller aerated mixer over the range of agitation used.

To estimate the values of χ, $C_{H,L}$ and $C_{C,L}$ from equations above, solubilities and mass transfer coefficients need to be known. The mass transfer coefficient for carbon monoxide was measured by Deckwer, et al. (1980) to be 0.010 cm/s and verified by them with Calderbank and Moo-Young's (1961) small-bubble correlation, using diffusivities estimated from a relation proposed by Sovova (1976). From these expressions, the dependence of the mass transfer coefficient on molar volume V_B can be deduced from which the mass transfer coefficient for hydrogen can be calculated as:

$$k_{L,H} = k_{L,C} (V_{B,C}/V_{B,H})^{0.4} \quad . \qquad (10)$$

Using molar volumes of hydrogen and carbon monoxide of 14.3 and 30.7 cm^3/mol respectively (Satterfield, 1970), $k_{L,H}$ becomes 0.014 cm/s. However, with little experimental data available, estimated values of these mass transfer coefficients have varied widely. Deckwer, et al. (1981) assumed a value $k_{L,H} = 0.02$ cm/s and Satterfield and Huff (1980) employed a value of 0.024 cm/s, based on early

literature, as opposed to $k_{L,H}$ = 0.014 cm/s used in this study. Stern et al. (1981) estimated the hydrogen and carbon monoxide mass transfer coefficients to be 0.21 and 0.019 cm/s, respectively, based on experimental parameters from a variety of sources. We have taken values of m_H = 2.04 x 10^5 cm^3 liq-atm/mol and m_C = 1.68 x 10^5 from Kölbel et al. (1955). Thus, calculated values of a in Fig. 3 vary from about 1 to 25 cm^{-1} at 200 to 400 RPM, respectively, assuming a gas hold-up of 0.2 and a hydrogen mass transfer coefficient of 0.014 cm/s.

Product Selectivity: Under intrinsic kinetic conditions the ratio of paraffins to olefins (α plus β), P/O, increases with hydrogen liquid-phase concentration, but is independent of CO concentration over a wide range of conditions (Satterfield and Huff (1982-a)). Thus it is the H_2 concentration at the liquid-solid interface that is important, not the H_2/CO ratio, which has been the focus of attention in some other analyses. This is illustrated in Figures 4 and 5 for the C_3 and C_7 fractions of the product, respectively, for two different experimental runs. In each of these, intrinsic kinetic data were obtained over a variety of pressures, H_2/CO feed ratios and feed rates. The CO concentration in the liquid varied more than 20-fold but there was no effect on the P/O ratio. This is developed in more detail elsewhere (Satterfield and Huff (1982-a)), but this conclusion is shown in the figures by displaying (in parentheses) the range of CO concentration for various convenient groups of data points. The P/O ratio increases approximately as the square root of hydrogen concentration. The C_3 and C_7 hydrocarbons are taken here as convenient measures of the P/O ratio in representative product fractions. The P/O ratio in general increased with molecular weight.

Paraffin to olefin molar ratios for the C_3 and C_7 fractions are reported in Table I for two sets of runs in which the degree of mass transfer was varied by varying RPM. Even with a CSTR, data on the effect of mass transfer must be interpreted carefully. An increase in mass transfer resistance, caused by decreased agitation, causes a drop in conversion. Usually the consumption ratio of H_2/CO is different than the feed ratio and hence a drop in conversion is accompanied by a change in the H_2/CO ratio in the gas present. Thus one must be careful to separate the effect upon the H_2 and CO concentrations in the liquid caused by change in conversion from that caused by mass transfer.

In the first set of runs in Table I, the H_2/CO feed ratio exceeds the consumption ratio, 7/12 = 0.58; in the second it is less than the consumption ratio. In each case, the H_2 partial pressure in the reactor increased with decreased agitation, as conversion dropped. In the absence of mass transfer resistance this would be expected to increase the P/O ratio. The fact that the P/O ratio in both cases instead decreased is consistent with the postulate that the H_2 concentration in the liquid has decreased. The corresponding mass transfer resistance $ℛ$, back-calculated from equation (8), is given at each stirring speed together with the hydrogen and carbon monoxide liquid-phase concentrations that are estimated by equations (6) and (7).

The H_2/CO feed ratios used here were chosen to be unusually low, so that the hydrogen liquid phase concentrations would be low, where selectivity effects caused by mass transfer should be more noticeable. In general, however, considerably higher H_2/CO feed ratios are usually used to minimize carbon formation so the feed ratio of H_2/CO generally exceeds the usage ratio. Hence under mass-transfer limited conditions the reaction becomes particularly starved for carbon monoxide since it is transported more slowly than hydrogen ($k_{L,C}$ = $k_{L,H}$/1.4) and it is the stoichiometrically-limiting reactant.

The paraffin to olefin ratios taken in a mass-transfer limiting environment

are also plotted in Figures 4 and 5 against predicted hydrogen liquid-phase con-
centrations. While the mass transfer results are within the data scatter on the
figures, we appear to underestimate the liquid-phase concentration slightly.
Perhaps this is due to a slight positive dependency of the intrinsic expres-
sion (Equation 2) on carbon monoxide and not zero order. This would result
in a higher back-calculated value of χ (and thus higher liquid-phase hydrogen
concentration) as carbon monoxide is transported slower than hydrogen. This
effect would be magnified by choosing too small a hydrogen mass transfer
coefficient.

The average product molecular weight is unaffected by stirring speed,
as evidenced by the ratio of C_1 to C_5 hydrocarbons in Table I. This is not
surprising as we have observed with intrinsic studies that this is relatively
independent of reaction conditions (Satterfield and Huff, 1982-b). However,
an increased H_2/CO liquid-phase ratio due to mass transfer limitations should
markedly decrease free carbon deposition by the Boudouard reaction (Satterfield
and Huff, 1982-c).

Conclusions: With an active fused-iron catalyst in a stirred autoclave reactor
we have shown that substantial mass transfer resistances are readily encountered
that greatly lower the observed reaction rate below that otherwise attainable.
Under intrinsic reaction conditions the paraffin to olefin ratio of the hydro-
carbon products is approximately proportional to the half-power of the hydrogen
concentration and is independent of CO concentration. Under mass-transfer
limiting conditions this P/O ratio dropped, in accordance with theory. Although
the gradient for hydrogen transfer is less than the gradient for CO transfer,
it is the hydrogen liquid-phase concentration that governs this selectivity
and not the H_2/CO ratio as such, as has been assumed in some previous analyses.
This is because of the form of the kinetic expression that governs paraffin-olefin
selectivity.

Under intrinsic-kinetic conditions the carbon number distribution of
products from a fused iron catalyst is not significantly affected by wide
variations in H_2 and CO concentration and mass-transfer resistances have no
noticeable effect, as would be expected. To the extent that other selectivities,
such as oxygenate product composition, are governed by H_2 and CO concentrations
in the liquid, we would similarly expect to observe effects caused by mass
transfer, although this was r·t done here. Likewise with other catalysts,
such as cobalt, which appear to be more sensitive to reaction conditions and
to secondary reactions, more marked effects from significant mass transfer
reactions are anticipated.

Table I. Effect of Mass Transfer on Selectivity at 243°C and 1.1 MPa.

Stirring Speed, N RPM	$(-R_{H_2+CO}) \times 10^7$ mol/s-cm³ liq.	$P_{C,atm}$	$P_{H,atm}$	$\frac{C_3^-}{C_3^-}$	$\frac{n-C_7^-}{n-C_7^-}$	$\frac{C_1}{C_5}$	χ s⁻¹	$k_c C_{C,L}$ atm	$k_H C_{H,L}$ atm
				$(H_2/CO)_{feed} = 0.62$					
600	7.45	4.08	2.98	.182	.268	5.13	—	4.08	2.98
400	7.12	4.25	2.97	.176	.258	5.72	.44	4.00	2.85
300	6.00	5.05	3.41	.169	.258	5.56	.045	3.06	2.41
250	5.03	5.34	3.55	.161	.241	6.62	.025	2.35	2.04
200	4.20	5.69	3.71	.148	.237	5.31	.016	1.79	1.74
				$(H_2/CO)_{feed} = 0.34$					
600	4.81	7.21	1.72	.139	.199	4.10	—	7.21	1.72
400	4.66	7.24	1.72	.136	.198	3.82	.63	7.13	1.67
300	4.20	7.41	1.82	.131	.197	4.21	.083	6.65	1.50
200	3.21	7.61	2.13	.130	.194	3.73	.025	5.70	1.16

Nomenclature

a   interfacial area of gas bubbles, cm^2 bubble surface area/cm^3 expanded liquid

c_L concentration in liquid phase, mol/cm^3 liquid; c_L^* for concentration at equilibrium with the gas, mol/cm^3 liquid

k_L liquid film mass transfer coefficient, cm^3 liquid/cm^2 bubble surface area - s

k   intrinsic reaction rate constant, s^{-1}

k_O overall apparent rate constant, s^{-1}

m   solubility coefficient, cm^3 liquid-atm/mol

N   stirrer speed, RPM

P   partial pressure, atm

-R   rate of reaction per unit volume of slurry, mol/cm^3 liquid - s

T   absolute temperature, °K

V_B molar volume of gas, cm^3/mol

Greek

ε_G gas hold-up, cm^3 gas/cm^3 expanded liquid; $1 - \varepsilon_G$ for liquid hold-up, cm^3 liquid/cm^3 expanded liquid

$\varkappa$ $\varkappa = k_{L,H} \, a/(1-\varepsilon_G)$, s^{-1}

Subscripts

C   carbon monoxide

H   hydrogen

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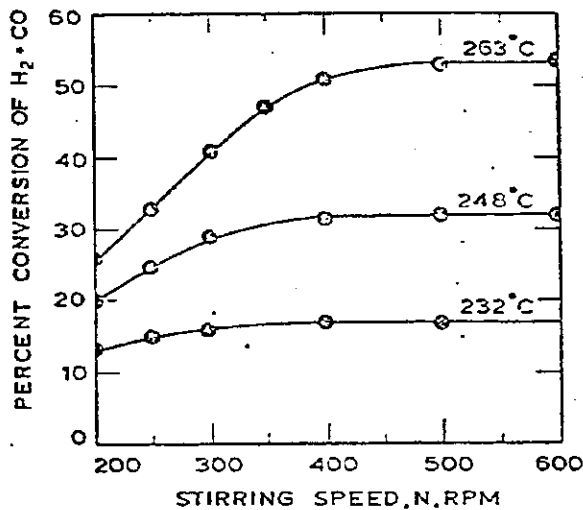Westerterp, K.R., L.L. Van Dierendonck, and J.R. De Kraa, Chem. Eng. Sci., 18, 157 (1963).

Figure 1. Effect of Stirring Speed on
Synthesis Gas Conversion;
790 kPa; 150 ℓ gas (S.T.P.)/ℓ liquid-hr;
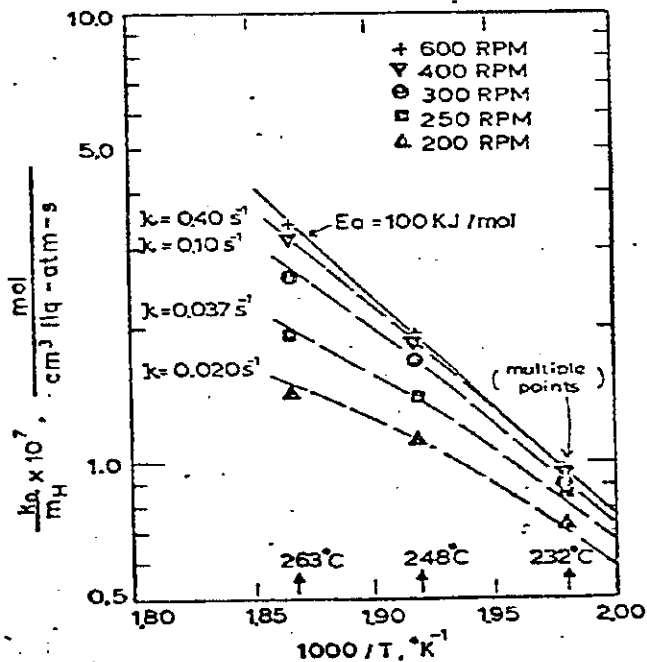$(H_2/CO)_{feed} = 0.69$.

Figure 2. Observed Rate Constant for same data points
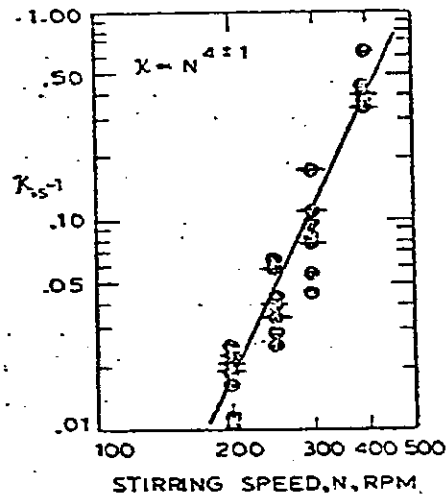as Fig. 1; 790 kPa; 150ℓ gas (S.T.P.)/ℓ liquid-hr;
$(H_2/CO)_{feed} = 0.69$.

Figure 3. Effect of Stirring Speed on Mass Transfer
Resistance, χ .

Solid shaft stirrer. Same data points as Fig. 1.
790 kPa; $(H_2/CO)_{feed} = 0.69$; 232 to 263°C.

Hollow shaft stirrer. 248 to 263°C;
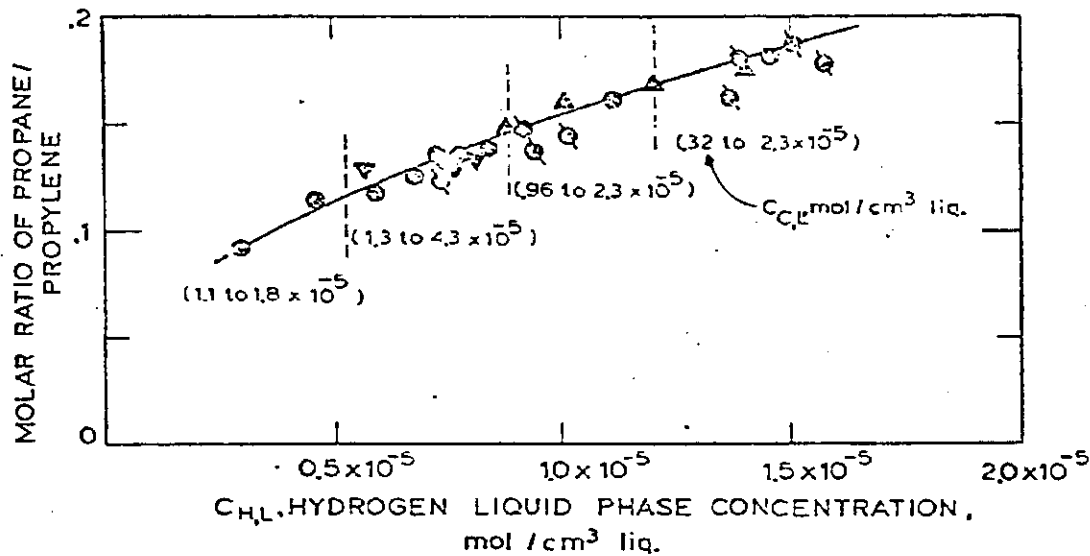400 to 1140 kPa; $(H_2/CO)_{feed} =$
0.34 to 0.62.

Figure 4. Propane to Propylene ratio in intrinsic and mass transfer-limited regions; 248°C.

Intrinsic
- Run 1: H_2/CO feed = 0.55-1.8; 400-790 kPa; 60-180ℓ gas/ℓ liquid-hr.
- Run 2: H_2/CO feed = 0.34-0.62; 280-1140 kPa; 100ℓ gas/ℓ liquid-hr.

Mass-Transfer
- Run 2: H_2/CO feed = 0.62; 1.1 MPa; 100ℓ gas/ℓ liquid-hr.
- Run 2: H_2/CO feed = 0.34; 1.1 MPa; 100ℓ gas/ℓ liquid-hr.

Figure 5. Heptane paraffin to olefin ratio in intrinsic and mass transfer-limited regions; 248°C.

Intrinsic
- Run 1: H_2/CO feed = 0.55-1.8; 400-790 kPa; 60-180ℓ gas/ℓ liquid-hr.
- Run 2: H_2/CO feed = 0.34-0.62; 280-1140 kPa; 100ℓ gas/ℓ liquid-hr.

Mass-Transfer
- Run 2: H_2/CO feed = 0.62; 1.1 MPa; 100ℓ gas/ℓ liquid-hr.
- Run 2: H_2/CO feed = 0.34; 1.1 MPa; 100ℓ gas/ℓ liquid-hr.