

Report 11

F-T SYNTHESIS IN SLURRY REACTOR SYSTEMS

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TITLE: Fischer-Tropsch Synthesis in Slurry Reactor Systems

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I. ABSTRACT

OBJECTIVE: A slurry-bed reactor for the Fischer-Tropsch synthesis offers several potential advantages over alternative modes of operation. These include the ability to operate at lower H_2/CO ratios, which can reduce the cost of preparing synthesis gas; excellent temperature control, the potential of achieving high conversion in a single pass, and a commercial reactor of simple construction. One objective of the proposed research is to establish a quantitative understanding of the mass transfer-related factors that determine selectivity and reaction rate in such a reactor. In addition, our mechanically-stirred autoclave can be operated as an isothermal CSTR, which provides a unique method of reliably comparing and contrasting different catalysts.

WORK DONE AND CONCLUSIONS: Our intrinsic reaction rate studies on a reduced fused magnetite catalyst, reported on last year, have now been published (Satterfield and Huff, J. Cat., 73, 187 (1982)).

We have studied the effects of mass transfer on catalytic activity and product selectivity by varying agitation rate. With a reduced fused magnetite catalyst a substantial gas-to-liquid mass transfer resistance can readily 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. A paper summarizing this study has been accepted for presentation at the Seventh International Symposium on Chemical Reaction Engineering, to be held in Boston in October 1982.

We are presently constructing equipment to study the effects of solids and solids loading on gas-liquid mass transfer. We tentatively plan to use a chemical method for measuring interfacial area in non-aqueous systems by reaction of carbon dioxide with various amines. This is analogous to the sulfite method used in determining interfacial areas in aqueous systems.

Dwyer and Somorjai, in a paper that has been widely quoted (J. Catal., 56, 49 (1979)), report that upon the addition of ethylene or propylene to synthesis gas, the value of α over an iron film catalyst increased dramatically. This implies that the olefin is incorporated into the

growing chains. We have now performed similar detailed studies with ethylene or 1-butene added to $\text{CO} + \text{H}_2$ on our reduced fused iron catalyst, but we can find no significant effect on α . Some of the ethylene is hydrogenated to ethane, but little hydrogenation of the butene occurred. The reasons for the difference in results is not clear, but may reside in differences between the form of iron we used and that of Dwyer and Somorjai.

As the result of some of our analyses, we conclude that the ability of a slurry-type Fischer-Tropsch reactor to process satisfactorily a feed synthesis gas of low H_2/CO ratio is intimately associated with a high degree of mixing in the reactor and the use of a catalyst active for the water-gas shift reaction. It is noteworthy that when the feed ratio exceeds the usage ratio in such a reactor, the highest degree of conversion results in the highest ratio of dissolved H_2 to CO in the liquid. This should minimize the extent of carbon formation and catalyst disintegration caused by disproportionation of CO . Thus high conversion is desired not only for economic performance but also to help maintain catalytic activity. This study is summarized in a paper by Satterfield and Huff (Can. J. Chem. Eng., 60, 159 (1982)).

From light product distribution data reported in previous slurry reactor studies with an iron catalyst, we calculate values of α to vary from 0.55 to 0.94. α is very sensitive to alkali content of the catalyst, reaction temperature to a lesser extent, but is relatively unaffected by pressure and gas composition. This analysis, by Satterfield, Huff and Longwell, will be published in Ind. Eng. Chem., Process Design Develop., July 1982. We are finding however, from our own work, that the product distribution for fused iron over a wide range of molecular weights is best fitted by two values of α . A value of about 0.7 applies to lighter products and a value of about 0.93 applies to waxes and heavy products. Fused iron may exhibit two kinds of sites with considerably different kinetic behaviour.

SIGNIFICANCE TO FOSSIL ENERGY PROGRAM: A liquid-phase Fischer-Tropsch process is a promising route for conversion of carbonaceous sources such as coal to liquid transportation fuels. However, in order to achieve maximum selectivity and activity, there must be an adequate understanding of the effect of mass transfer on the nature and distribution of products. Further, the stirred autoclave system developed provides a unique method of comparing catalysts under isothermal intrinsic kinetic conditions.

PLANS FOR THE COMING YEAR: Studies with a precipitated iron and an iron-manganese catalyst are planned for comparison with the fused iron catalyst. Studies with cobalt and ruthenium catalysts will follow. Experimental results of the effects of solids on gas-liquid mass transfer should start to be forthcoming within 3 to 6 months. Effects of mass transfer on product selectivity will be pursued with the groups of catalysts to be studied.

II. HIGHLIGHT ACCOMPLISHMENTS

On a fused magnetite catalyst, mass transfer limitations cause an increase in the olefin-paraffin ratio of the products. With this catalyst, the addition of ethylene to synthesis gas caused no noticeable change in α , in contrast to work reported by others on another type of iron catalyst. We conclude that the ability of a slurry-type Fischer-Tropsch reactor to process satisfactorily a feed synthesis gas of low H_2/CO ratio is intimately associated with a high degree of mixing in the reactor and the use of a catalyst active for the water-gas shift reaction.

Fischer-Tropsch Synthesis in
Slurry Reactor Systems
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FISCHER-TROPSCH SYNTHESIS IN
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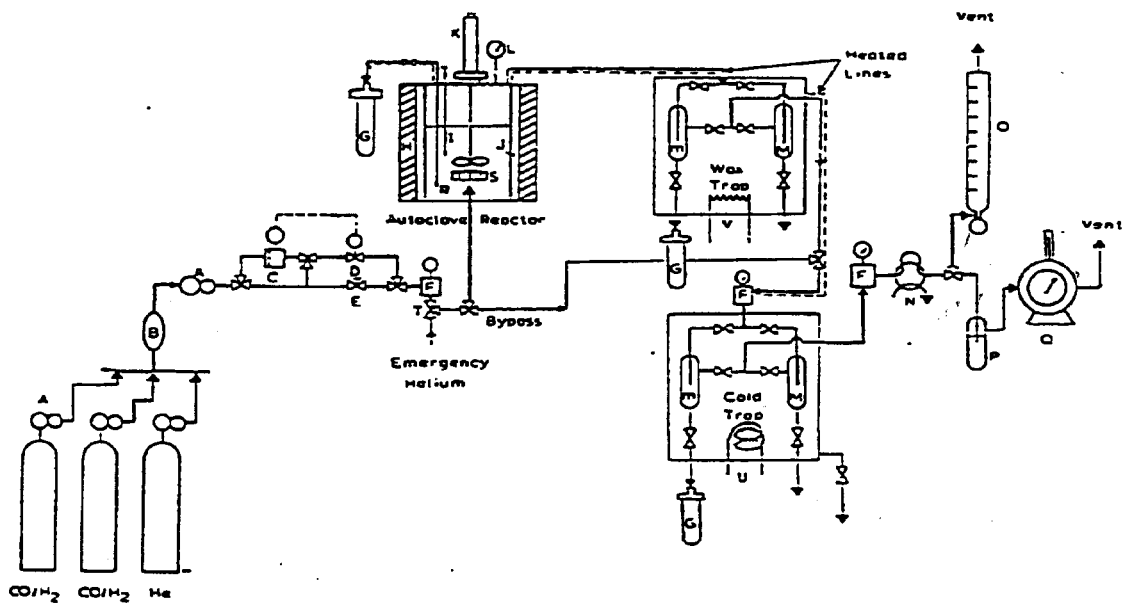
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C. N. SATTERFIELD

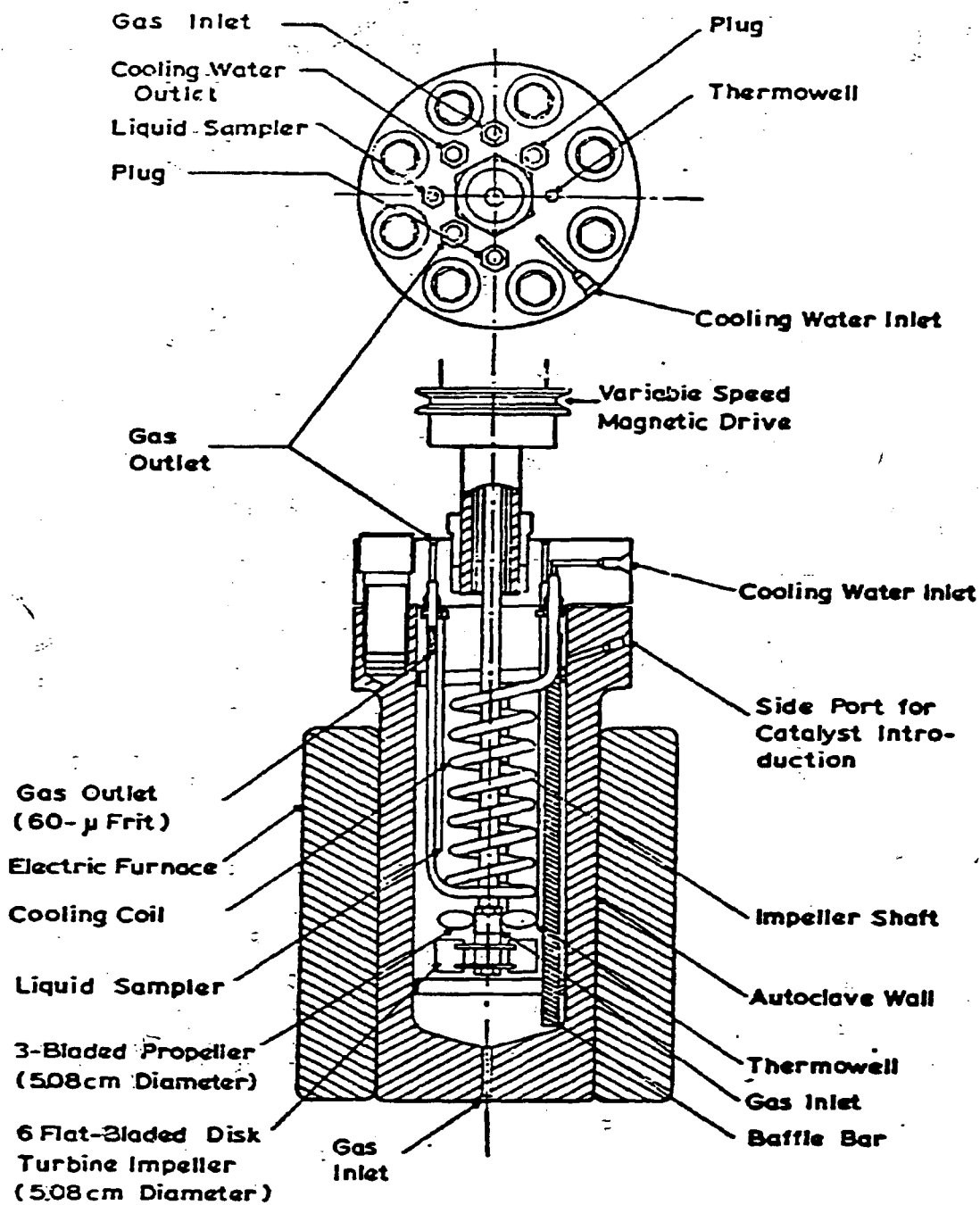
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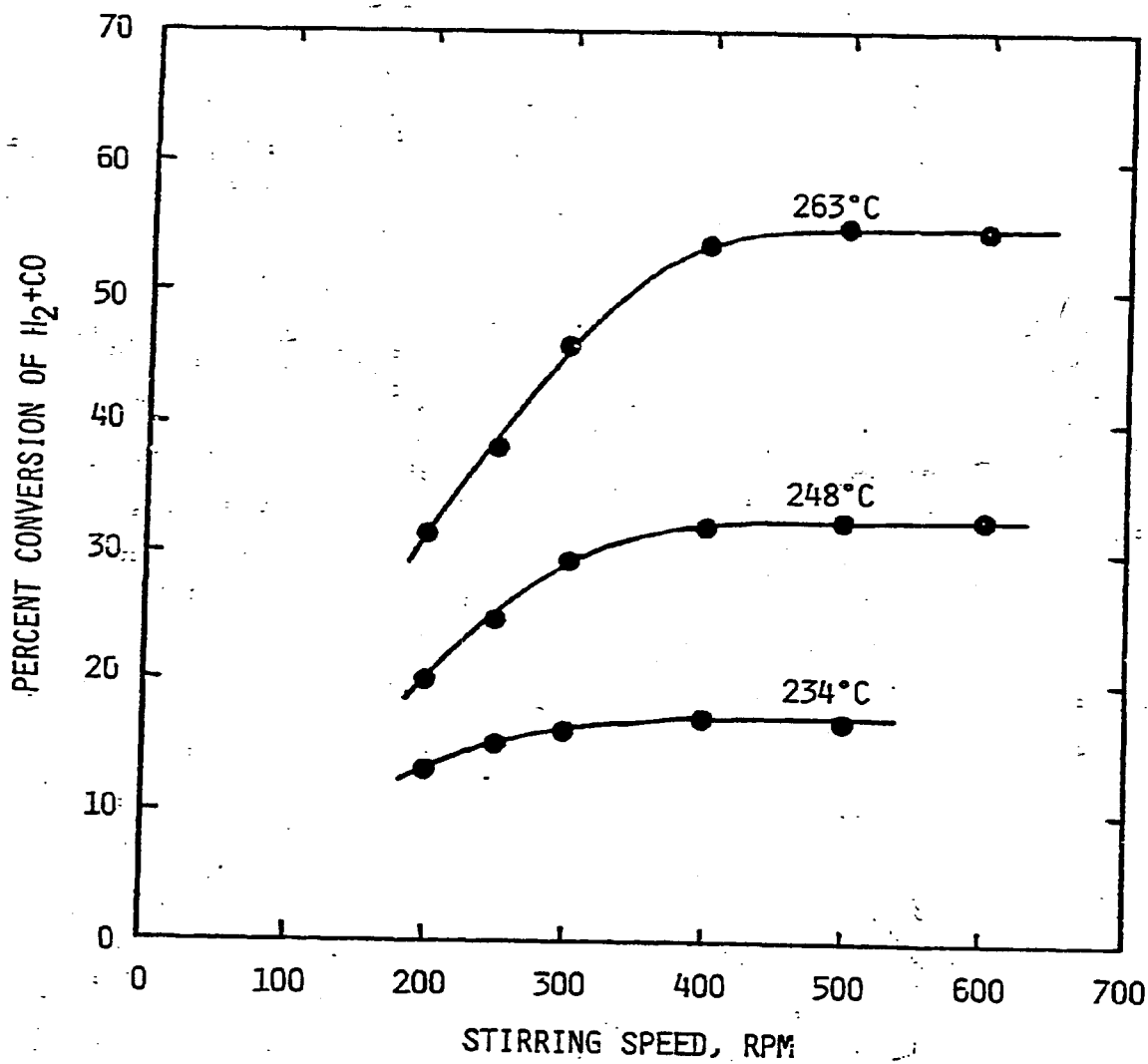
1. ADVANTAGES OF SLURRY REACTOR SYSTEMS
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4. EVIDENCE FOR A DOUBLE α

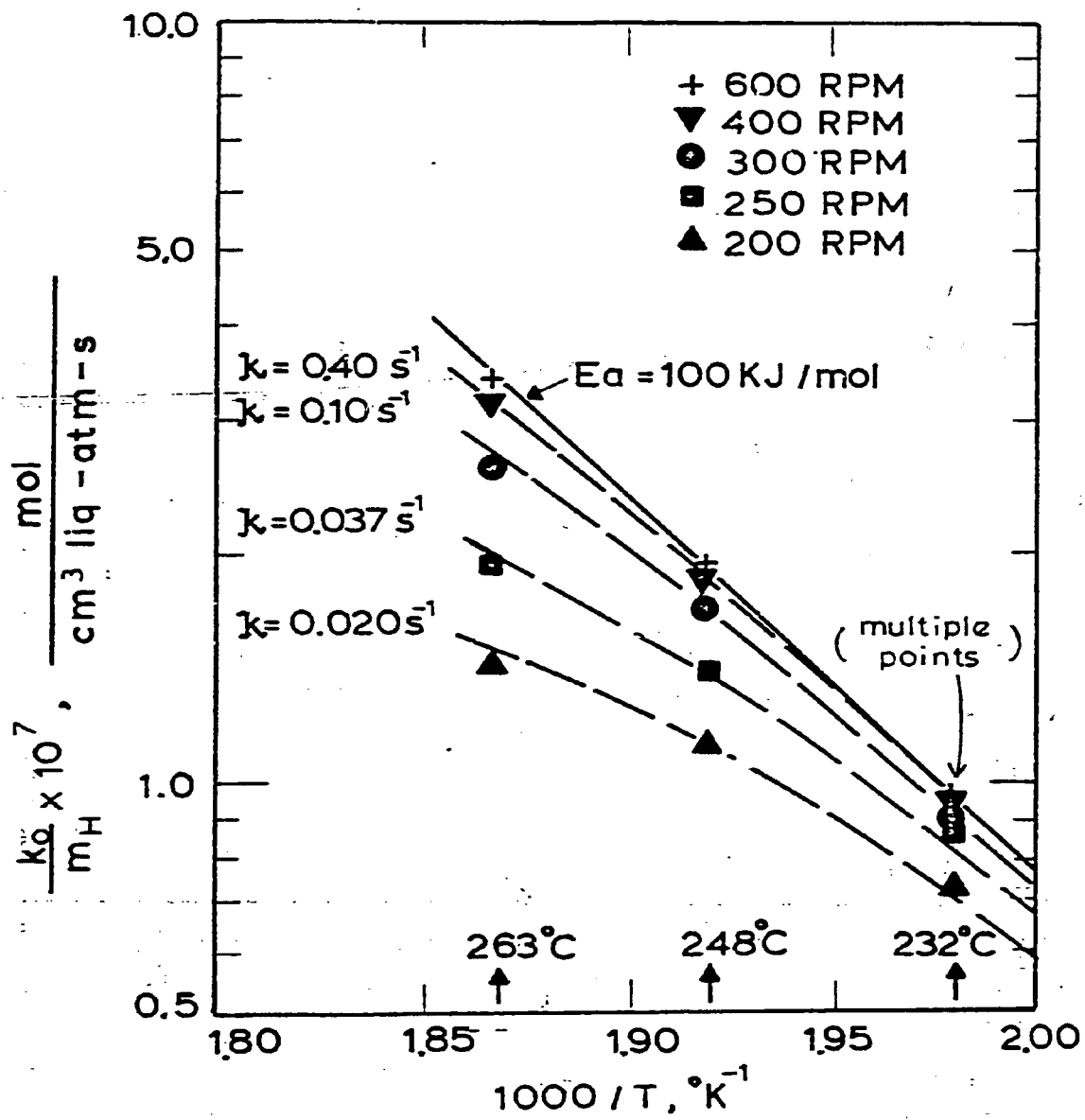
POTENTIAL ADVANTAGES

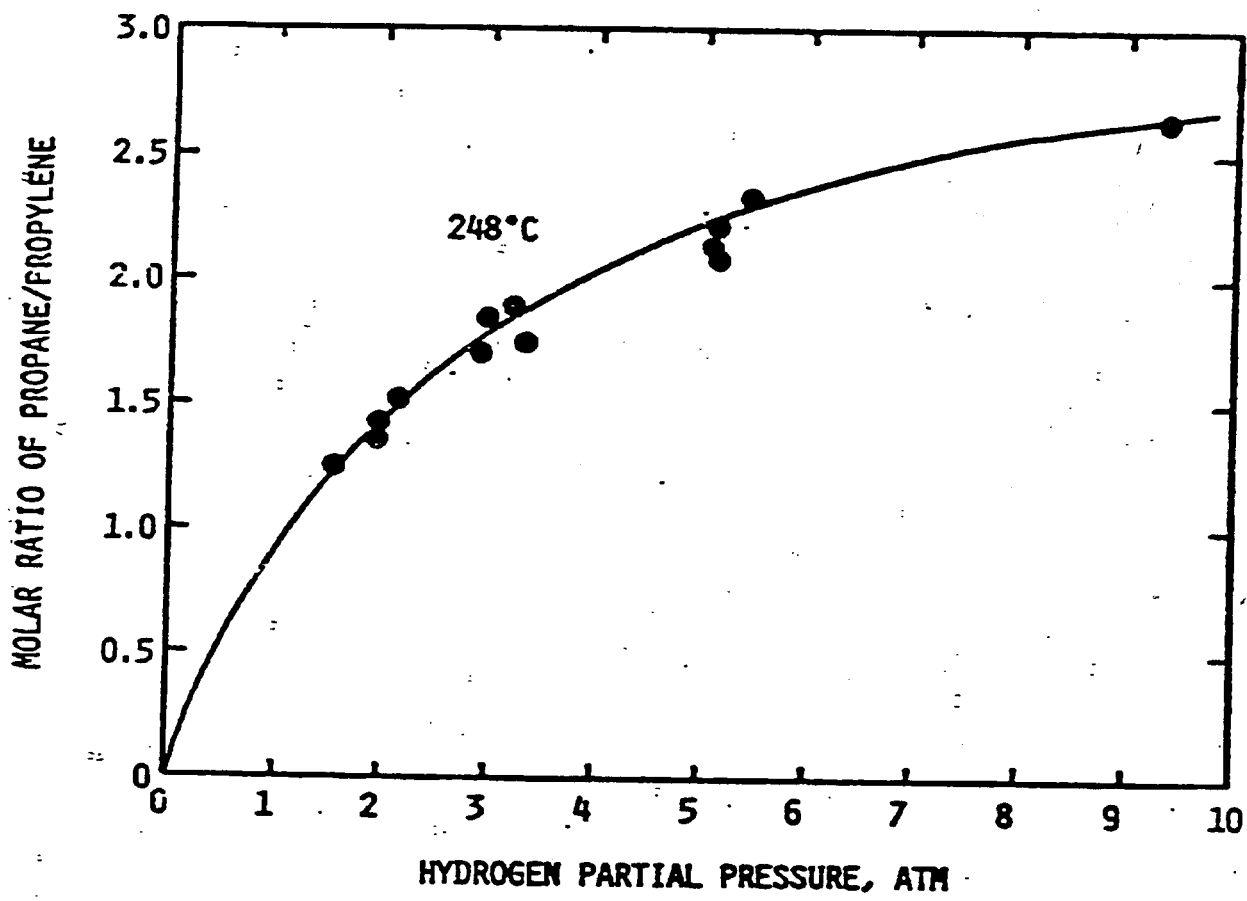
- DESORPTION OF HIGH MOLECULAR WEIGHT PRODUCTS
- LONGER-LIVED CATALYST
- GOOD TEMPERATURE CONTROL
- OPERABLE OVER WIDE RANGE OF H_2/CO RATIOS
- EASE OF HEAT RECOVERY
- HIGH CONVERSION IN SINGLE PASS IS POSSIBLE
- GOOD MIXING PLUS INTERNAL WATER GAS SHIFT GIVES HIGH H_2/CO RATIO. THEREFORE HIGH RATE AND LOW CARBON FORMATION.
- GOOD TEMPERATURE CONTROL AND C.S.T.R. BEHAVIOUR CAN PROVIDE EXCELLENT INTRINSIC KINETIC DATA.

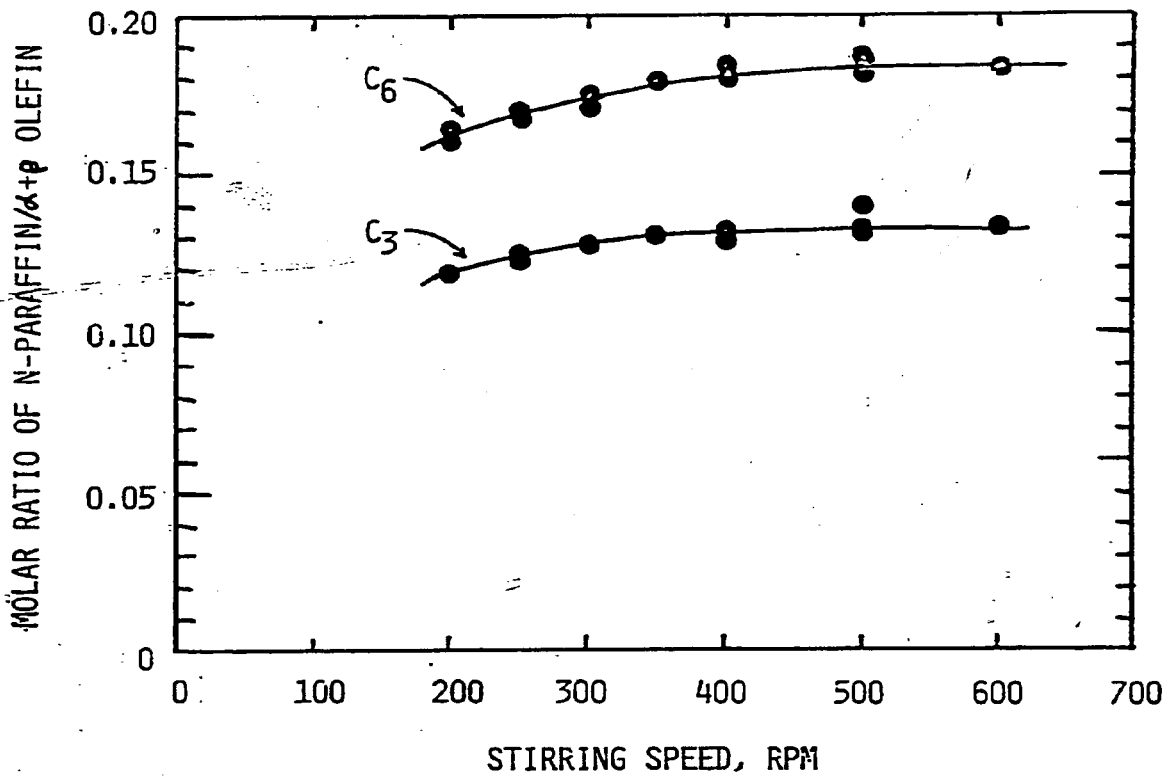




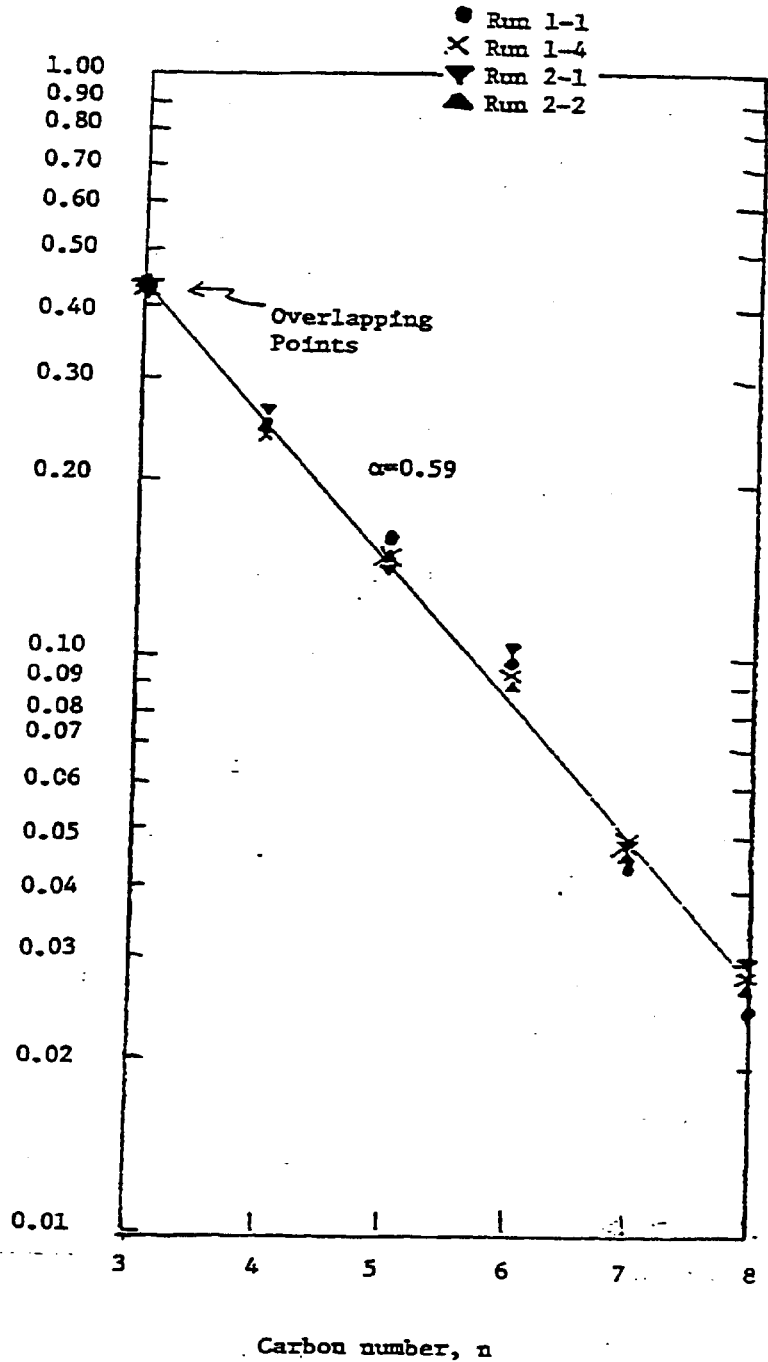




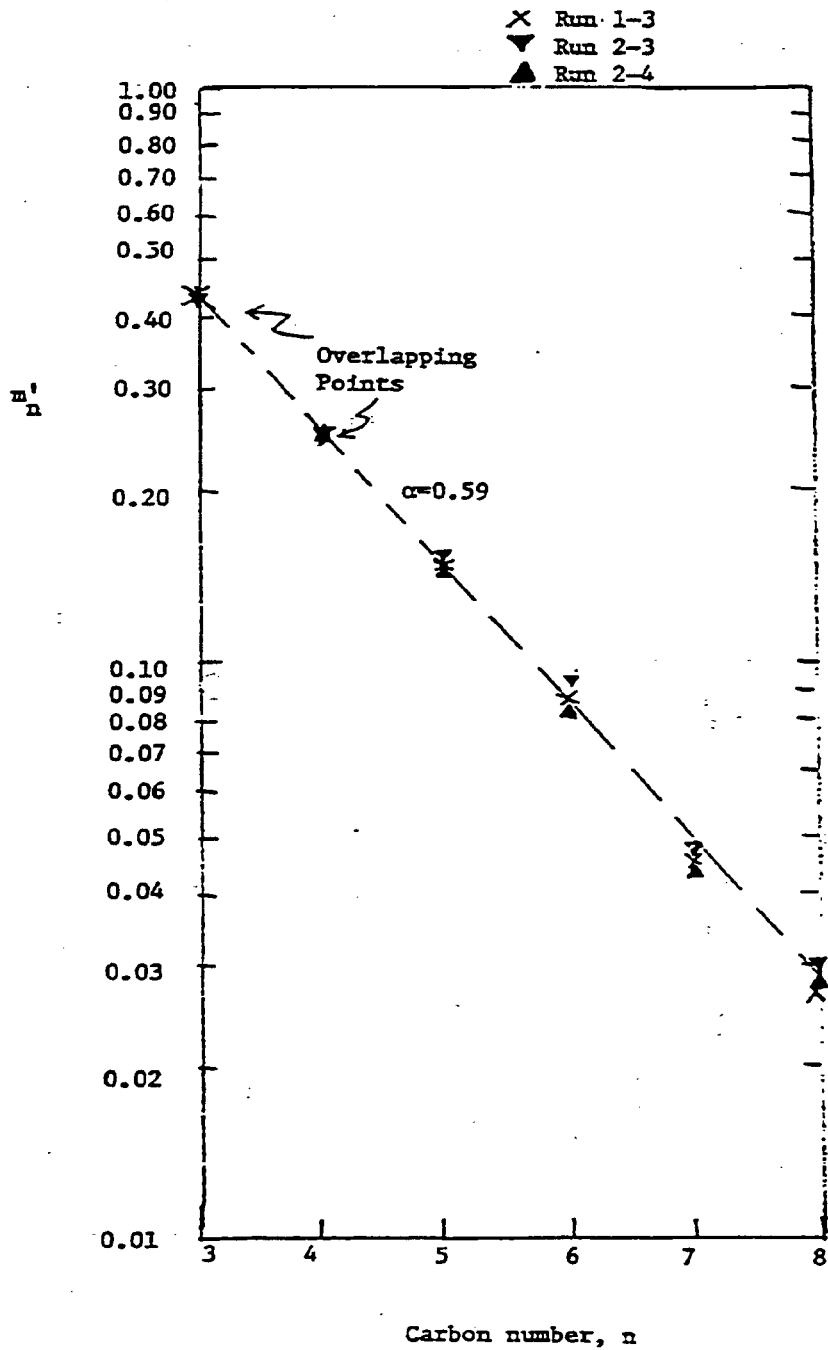




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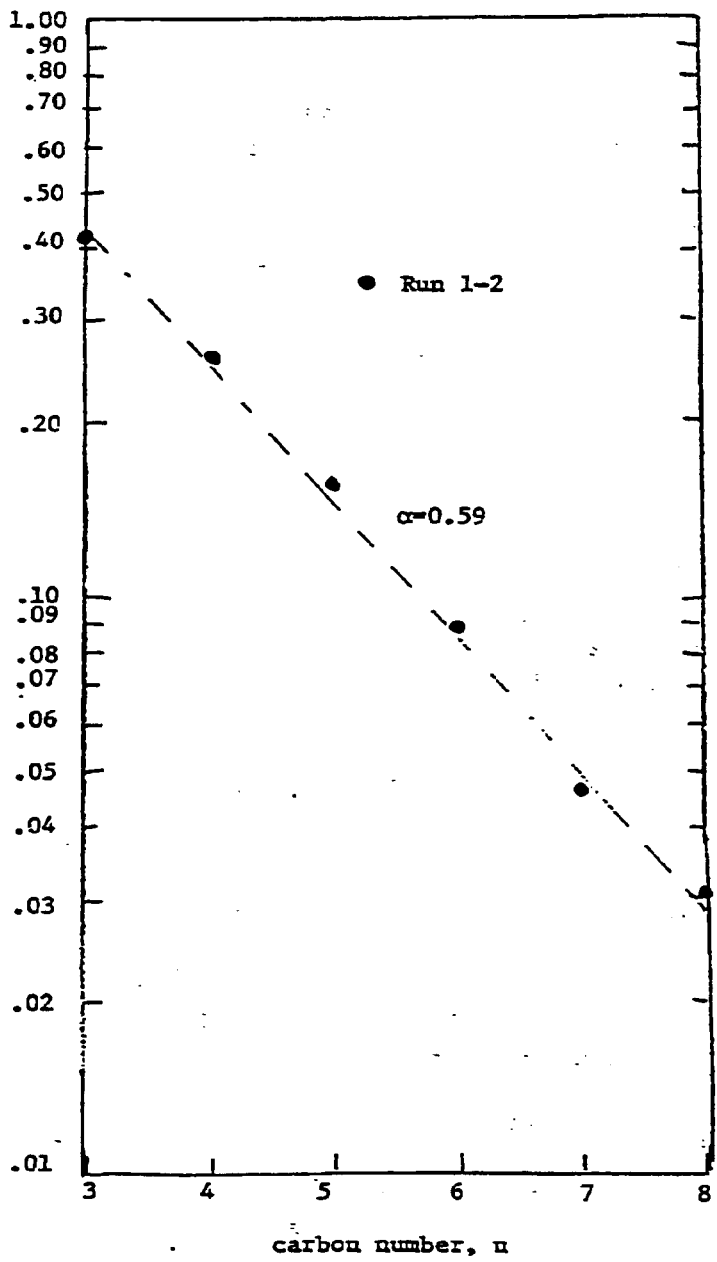


Flory Distribution.
Synthesis Gas Alone.

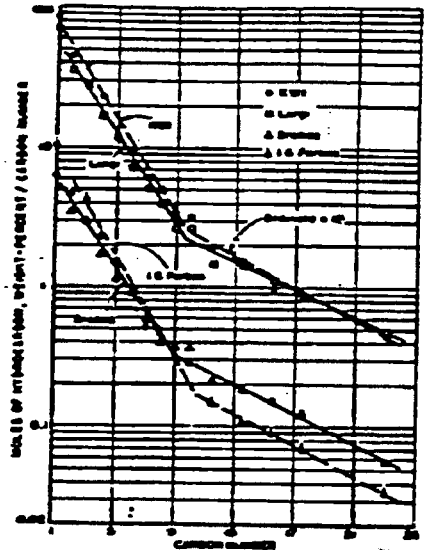


Flory Distribution
 1.5 mole% Ethylene Added to the
 Synthesis Gas
 11-14

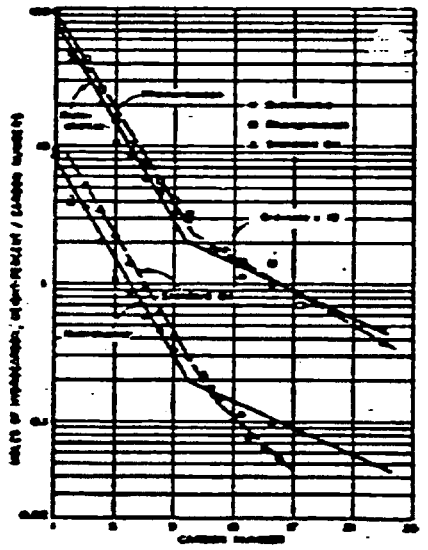
H_n



Flory Distribution
0.86 mole% 1-butene added to
the synthesis gas.



Logarithmic plots of moles against carbon number for hydrocarbons from Schwarzschild tests.



Logarithmic plots of moles against carbon number. Hydrocarbons from Schwarzschild tests compared with those from fluidized synthesis.

