TECHNOLOGY DEVELOPMENT FOR IRON FISCHER-TROPSCH CATALYSIS

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Abstract

The goal of the proposed work is the development of iron-based Fischer-Tropsch catalysts that combined high activity, selectivity and life with physical robustness for slurry phase reactors that will produce either low-alpha or high-alpha products. The catalyst that is developed will be suitable for testing at the Advanced Fuels Development Facility at LaPorte, Texas or similar sized plant. Previous work by the offeror has produced a catalyst formulation that is 1.5 times as active as the "standard-catalyst" developed by German workers for slurry phase synthesis. The proposed work will optimize the catalyst composition and pretreatment operation for this low-alpha catalyst. In parallel, work will be conducted to design a high-alpha iron catalyst that is suitable for slurry phase synthesis. Studies will be conducted to define the chemical phases present at various stages of the pretreatment and synthesis stages and to define the course of these changes. The oxidation/reduction cycles that are anticipated to occur in large, commercial reactors will be studied at the laboratory scale. Catalyst performance will be determined for

catalysts synthesized in this program for activity, selectivity and aging characteristics.

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1.0 Executive Summary

The performance of an iron-based catalyst for the Fischer-Tropsch synthesis has been analyzed for the purpose of increasing the hydrocarbon production rate. Syngas conversion rates are high at low conversion levels and continuously decrease at higher conversion levels. Further, a comparison of the relative reaction rates of the Fischer-Tropsch synthesis and the water gas shift reaction indicate that the fraction of CO converted to hydrocarbons is also higher at lower conversion levels. This indicates that it is beneficial from a hydrocarbon productivity standpoint to limit the syngas conversion in the reactor to a lower value. Higher overall syngas conversions can be achieved by either recycling the unconverted syngas back to the reactor or by having two or more reactors in series. The hydrocarbon space time yield is, for instance, doubled by using a recycle reactor with 67% syngas conversion per pass versus a single pass reactor operated at 90% syngas conversion.

Currently a dominant viewpoint is that a high-alpha Fischer-Tropsch catalyst is required to produce transportation fuels. The high amounts of wax produced by such a catalyst is subsequently hydrocracked to increase the yield of diesel range hydrocarbons. However, it is pointed out that in both cases (especially important for the low alpha case), the use of an oligomerization unit is needed to transform the light hydrocarbons (usually gas phase) into liquid fuels, in this case gasoline. Thus the difference between the downstream processing of products obtained from a low-alpha versus a high-alpha catalyst is merely in the relative sizes of the hydrocracking and oligomerization reactors. Moreover there is a substantial advantage in the operation of a slurry reactor with the use of a low-alpha catalyst. There is little accumulation of wax in the reactor thereby minimizing the difficulty of separating the catalyst from the wax. In addition small catalyst particles can be used, simplifying the catalyst preparation procedure.

In summary, it appears that it would be appropriate to make a process and economic evaluation for both the low and high alpha iron catalysts. It also appears that a similar assessment should be made to identify the conversion level that would be most suitable for taking advantage of the selectivity of the iron catalyst.

2.0 Introduction

The objective of this research project is to develop the technology for the production of physically robust iron-based Fischer-Tropsch catalysts that have suitable activity, selectivity and stability to be used in the slurry phase synthesis reactor development. The catalysts that are developed shall be suitable for testing in the Advanced Fuels Development Facility at LaPorte, Texas, to produce either low- or high-alpha product distributions. Previous work by the offeror has produced a catalyst formulation that is 1.5 times as active as the "standard-catalyst" developed by German workers for slurry phase synthesis. The proposed work will optimize the catalyst composition and pretreatment operation for this low-alpha catalyst. In parallel, work will be conducted to design a high-alpha iron catalyst this is suitable for slurry phase synthesis. Studies will be conducted to define the chemical phases present at various stages of the pretreatment and synthesis stages and to define the course of these changes. The oxidation/reduction cycles that are anticipated to occur in large, commercial reactors will be studied at the laboratory scale. Catalyst performance will be determined for catalysts synthesized in this program for activity, selectivity and aging characteristics.

The research is divided into four major topical areas: (a) catalyst preparation and characterization, (b) product characterization, (c) reactor operations, and (d) data assessment.

To accomplish the objectives of the project, these topics have been organized into the following technical tasks:

a. Task 1.0 Development of Optimum Promoter Levels for Low- and High-Alpha Catalysts

The goal of this task is to identify and optimize procedure for the preparation of iron-based catalysts that combine high activity selectivity and life with physical robustness. Each of the subtasks address an area of considerable uncertainty in the synthesis of catalysts.

1.1 Determine Optimized Synthesis Procedure for High-Alpha Iron-Based Fischer-Tropsch Catalysts

- Role of precursor particle size on activity.
- Role of Cu in precipitated catalysts.
- Define attrition resistance.

1.2 Prepare Catalysts that can be Used to Determine the Role of Promoters for Low- and High-Alpha Catalysts

- Define optimum SiO_2.
- Define optimum Al_2O_3.

1.3 Prepare Catalysts that can be Used to Quantify the Role of K on Product Selectivity in both Low- and High-Alpha Catalysts.

1.4 Complete the Optimization of the Two Best Low-Alpha, Iron-Based Fischer-Tropsch Catalysts Developed during the Previous Contract.

b. Task 2.0 Definition of Preferred Pretreatment for both Low- and High-Alpha Fischer-Tropsch Catalysts.

The goals of this task are to define the preferred treatment, to define the role of Cu and K during the pretreatment on activity and selectivity and to define the chemical and physical changes which occur during the preferred pretreatment. The subtasks address each of these goals.

2.1 Determine the Role of Cu in the Activation of Precipitated Low- and High-Alpha, Iron-Based Fischer-Tropsch Catalysts.

2.2 Determine the Effect of K Content on Activation Procedures and Determine if the Method of Addition has any Effect on Catalyst Activity and Life.

2.3 Determine the Physical and Chemical Changes that Occur during Catalyst Pretreatment and Use and Determine how these Changes Effect the Strength of the Catalysts.

2.4 Evaluate the Effect of Carbon Deposition during Catalyst Activation on Activity, Selectivity and Aging Characteristics.

c. Task 3.0 Catalyst Structure and Characterization.

The goal of this task is to provide basic analyses (surface area, XRD) of all catalyst prepared and to provide additional techniques as required (Mössbauer, SEM, XPS, etc.) to answer specific questions or to provide basic required characterization data for the catalysts.

d. Task 4.0 Catalyst Testing.

The goals of this task are to operate the eight CSTR reactors, measure catalyst performance, determine the stable phases that exist during synthesis at low and high conversions and to determine the rates of interconversion of iron oxide and carbide.

4.1 Verify the Quality of Data Obtained from the CSTR's.

4.2 Measure Catalyst Performance.

4.3 Determine the Stable Phases that Exist during Synthesis at Low and High CO Conversion Levels.

4.4 Obtain Data on the Rates Involved in the Interconversion of Iron Oxide and Iron Carbide.

Results and Discussion

The production of liquid fuels from coal is a desirable goal to reduce the dependence on crude oil imports. Indirect coal liquefaction is a promising approach to achieve this goal. Coal is first gasified to produce synthesis gas which is a mixture of carbon monoxide and hydrogen. Subsequently, the synthesis gas is converted to hydrocarbons by the Fischer-Tropsch Synthesis (FTS).

Advanced fluidized coal gasification processes produce a synthesis gas with a low H_2/CO ratio, represented by a value of about 0.67. The direct processing of this gas in the FTS eliminates the need for an additional step (water-gas shift) to increase the H_2/CO ratio. The inherent water gas shift activity possessed by iron FTS catalyst allows the direct processing of low H_2/CO ratio synthesis gas in the slurry reactor without excessive coking of the catalyst. Moreover, the slurry reactor is superior to the multi-tubular bed reactor in terms of temperature control.

The water gas shift (WGS) reaction occurs simultaneously with the production of hydrocarbons during the FTS over iron-based catalysts. These two reactions are shown below:

FTS:

$$nCO + 2nH_2 \text{ ----> } (-CH_2-)_n + nH_2O \qquad [1]$$

WGS:

$$CO + H_2O \text{ ----> } CO_2 + H_2 \qquad [2]$$

For a feed gas having an H_2/CO ratio of 0.67, the maximum obtainable conversion of CO without the WGS reaction is only 33%. This illustrates the desirability of a high rate for the WGS reaction. However, a high WGS reaction rate could convert a larger amount of CO (source of carbon) to CO_2 rather than the desired hydrocarbon products. However, from the mass balance point of view, the production of CO_2 parallels the production of H_2 and potentially increases the rate of reaction [1] so that it is not a loss as the CO and CO_2 are exchangeable through the water-gas shift reaction. Thus the relative extents of the FTS and WGS reactions need to be optimized for the maximum production of hydrocarbons. In this study the performance of an iron-based catalyst is analyzed from this viewpoint and alternative process/reactor configurations are suggested to improve the rate of production of hydrocarbons.

The FTS produces a large variety of hydrocarbons ranging from light gases to heavy wax. If the logarithm of the mole fractions of the various hydrocarbons are plotted against the number of carbon atoms a straight line is obtained (Anderson-Schulz-Flory (ASF) reaction mechanism). The slope of this straight line, termed alpha, uniquely describes the hydrocarbon selectivity. A high value of alpha implies greater production of heavy hydrocarbons while a low value of alpha implies a greater production of lighter hydrocarbons. A current viewpoint is that it is desirable to have a catalyst with a selectivity given by a high value of alpha (0.9 or greater). The higher amounts of heavy hydrocarbons produced can be subsequently processed in a hydrocracking unit to produce diesel range hydrocarbons. For example, this approach is being followed in the Shell Middle Distillate Synthesis (SMDS) process.[1] In this study we present an analysis of data from low- and high-alpha iron catalysts and compare the options for further processing of the hydrocarbon products obtained in both cases. Further, the low- and high-alpha catalysts are compared with respect to the operation of slurry FTS reactors.

Hydrocarbon Productivity

A consideration of the conversions of CO and H_2 versus the flow rate for a syngas typical of the product from a modern coal fluidized gasification unit (H_2/CO = 0.7) shows that conversion rates of synthesis gas decrease with increasing CO conversions;[1] a similar observation applies even when H_2/CO = 1.[2] For example, for the data shown in Figure 1 for a catalyst with an atomic composition of 100 Fe/4.4 Si/0.71 K, about 67% CO conversion is obtained at a flow rate of 10 NL/hr.-g(Fe); however, to increase the conversion to 90% in a single pass conversion process the flow rate must be decreased to about 3.1 NL/hr.-g(Fe). In other words, the process pays a significant price in the rate of the reaction in order to increase the conversion from 67 to 90% CO conversion using a single pass reactor. Further, along with the rate of syngas conversion, the rate of hydrocarbon production also decreases with increasing CO conversions (Figure 2).

Moreover, a consideration of the relative conversions of hydrogen and carbon monoxide shows that a significant fraction of the CO conversion goes to the production of CO_2 and excess hydrogen at the higher CO conversion levels. Figure 3, obtained from the same data as Figure 1, clearly shows that the lower CO conversion levels produce a higher fraction of hydrocarbons per unit CO conversion than for high CO conversion levels. This drop of the useful fraction of converted carbon can also be expressed by the drop of the usage ratio from 1.0 to 0.6.

The above considerations imply that it is beneficial to operate a Fischer-Tropsch reactor at lower CO conversions per single pass. This is further illustrated by considering the above data from the point of view of space time yield. This is shown below for a catalyst loading of 20% iron in the slurry and the conversion is based upon a normal liter of slurry volume. However, the same consideration applies for any catalyst loading and should be nearly independent of reactor size. For the iron catalyst prepared at the CAER (100Fe/4.4Si/0.71K atomic ratio) that was used to generate the data shown in Figure 1, the grams of CO converted per reactor volume are plotted in Figure 4 for increasing reaction times. It is seen that the rate decreases with reaction time (Figure 2) with a maximum being attained at low reaction times (0.025

hr.-g(Fe)/NL). The production of hydrocarbons also decreases with reaction time with a maximum at the same low reaction times (0.025 hr.-g(Fe)/NL) as shown in Figure 5. The production of CO_2 also decreases with reaction time (Figure 6) but the maximum occurs at intermediate values or reaction time (0.05 hr.-g(Fe)/NL). Thus, based upon the reactor productivity of hydrocarbons, the syngas space velocity should be high (40 NL/hr.-g(Fe)) for (1) the full utilization of the catalyst activity and (2) to obtain the maximum hydrocarbon production without excessive production of CO_2. This flow rate corresponds to a single pass CO conversion of 25% for the catalyst and reaction conditions used in this example.

Alternate Reactor Configurations

In order to take advantage of the higher reactor productivity at higher syngas flow rates and low single pass CO conversions, two options are available for designing a process: recycle of unconverted synthesis gas that exits the reactor or to utilize a number of reactors in series. In the following discussion we have arbitrarily chosen the point where the hydrogen and carbon monoxide conversions are equal (equivalence point) as the desired single pass (or single reactor) CO conversion level. This is for convenience, and the following general considerations would apply for other conversion levels. At the equivalence point the unconverted syngas that exits the reactor has the same chemical composition as the syngas fed to the reactor. The equivalence point for our catalyst is at 67% syngas conversion as shown in Figure 7. The equivalence point depends upon the catalyst (e.g., see ref. 2). Thus, the unconverted syngas exiting the reactor could be either recycled or used as a feed for another reactor without having to make any adjustments to either hydrogen or carbon monoxide content. It is recognized that the CO conversion level at the equivalence point is higher than the CO conversion for maximum reactor hydrocarbon productivity. However, the following discussion illustrates the increased hydrocarbon productivity obtained without the need for an additional supply of hydrogen or carbon monoxide. Furthermore, the following discussion is based solely upon what should be the most efficient use of the syngas and reactor volume. It is realized that this may not be the most efficient approach when considering the overall process.

For the catalyst that produces an equivalence point for the syngas exiting the reactor at 67% CO conversion, the reactor can be operated at a syngas flow of 10 NL/hr.-g(Fe). If we consider the option of a recycle reactor, one third of the inlet synthesis gas would remain unconverted and would be recycled. Of course, it would be necessary to remove the hydrocarbon products, CO_2 and H_2O from the vapor exiting the reactor prior to recycle of the unconverted syngas (Figure 8). The net result is, however, that recycle provides for essentially 100% conversion of the syngas at an effective flow rate of syngas of

6.7NL/hr-g(Fe) rather than the value of 3.1NL/hr-g(Fe) to attain 90% CO conversion. In addition, effecting the conversion of syngas at the lower conversion level favors hydrocarbon production over excess WGS. Thus, for the same slurry volume and catalyst loading, the recycle operation would produce about 2.1 times as much hydrocarbon per unit time as would be produced in the single pass process. This study considered the removal of CO_2 from the recycle stream. However, this step would increase the investment. Additional studies are needed to assess the equilibrium concentration of CO_2 in a loop with a stream that is continuouosly purged.

Another option for a process that takes advantage of the increased reaction rate and the hydrocarbon productivity that results from limiting the single pass conversion to the equivalence point is to use reactors in series. For a process that utilizes a series of reactors the simplest approach to accomplish greater than 90% CO conversion would be to use a second reactor that is approximately one-third the size of the first reactor. However, this approach would have the same disadvantage such as (1) the increase of design/engineering cost, (2) inability to interchange the reactors, and (3) having to stock different replacement components for the reactors. For these reasons, it would probably be preferred to utilize two or three reactors of the same size and to add sufficient syngas to the unconverted syngas exiting the previous reactor to obtain the required feed rate (Figure 9). A reviewer noted that another option would be to feed the effluent from several first-stage reactors to a single second-stage reactor.

Comparison of Low-Alpha and High-Alpha Catalysts

It appears to have become a common conception that a high alpha Fischer-Tropsch catalyst is needed for the production of transportation fuels. For example, the Shell Middle Distillate Synthesis (SMDS) process utilizes a high alpha Fischer-Tropsch cobalt catalyst with a chain-length-independent FT chain-growth reaction and a chain-length-dependent cracking process.[1] This permits the products to be optimized at the middle distillate range.

It appears, however, that a process utilizing either the low or the high alpha Fischer-Tropsch iron catalyst would require both an oligomerization and a hydrocracking unit (Figure 10) to increase the yields of gasoline and diesel. The major difference between the two options, low or high alpha catalysts, would be the relative sizes of the oligomerization and the hydrocracking units. For the present consideration, we utilize data generated by Mobil utilizing the slurry phase reactor,[3] and the appropriate data yield are reproduced in Table 1.

Table 1

Product Yield for an Iron Catalyst Operated in the Low and High-alpha Mode[4]

Conditions	Low-Alpha Catalyst	High-Alpha Catalyst
Temperature (°C)	260	258
Pressure (atm)	15	15
SV ($NLh^{-1}g^{-1}(Fe)$)	2.6	2.4
H_2/CO	0.67	0.67
Activity		
$CO + H_2$ Conv., %	86.8	82.2
$Nm^3(kg\ Fe)^{-1}h^{-1}$	2.25	1.97
Selectivity		
C_1	7.8	2.7
C_2-C_4	24.5	11.1
C_5-C_{11}	41.9	18.1
C_{12+}	26.2	68.1

First, it is noted that the activity and the hydrocarbon productivity rate are similar for the two catalyst options, but slightly favors the low-alpha option. In both process options, too much of the products fall in the C_2-C_4 range for these products to be discarded; thus, these would be utilized to produce liquid transportation fuels, most likely using an oligomerization process. It is also possible to utilize the C_2 - C_4 olefins as a chemical feedstock, thereby commanding a premium value until sufficient reactors are constructed to cause an oversupply of C_{2-4} olefins. While the heavier products are not broken down into middle distillate and wax in the above table, both process options would produce some wax. Thus, both processes would require some cracking facility, most likely a hydrocracking process. For the above example, the oligomerization unit for the low-alpha process would need to be about twice the size of the one for the high-alpha process. On the other hand, it would certainly require a much larger hydrocracking unit (2 to 5 times) for the high-alpha process than for the low-alpha process. In general, the cost of construction of a medium or high pressure hydrocracking process ($2000-4000/bpsd)[5] is about the same as that required for an oligomerization process ($2500-4000/bpsd).[6] On the other hand, while some methane and ethane would be produced by the hydrocracking process, it is likely that the low-alpha process would produce more of these two gases than the high-alpha process.

For the U.S., gasoline is currently a dominant fraction of the transportation fuel market. The low alpha catalyst produces gasoline (65-75 wt.%) as the major product. Furthermore, Kölbel and co-workers[7] reported that the gasoline containing the oligomers from the C_2-C_4 fraction has an octane number of 83, a value surprisingly close to the value of 87 currently marketed in the U.S. as suitable for use in most autos. It is realized that a major reason for the high octane rating of the product referred to by Kölbel and coworkers[7] was the alkene content, and that alkenes are not a desirable component of today's gasoline. Even so, it appears that iron catalysts with both low and high alpha values should be considered in a process that utilizes Fischer-Tropsch Synthesis to produce transportation fuels. It appears that the expense of producing the larger amount of low value methane and ethane with a low alpha catalyst may be less than the expense of hydrocracking the heavy wax produced by the high alpha catalyst and the smaller fraction and poorer quality gasoline that is produced by the hydrocracking process.

Operation of Slurry Reactor with Low-alpha Catalyst

For the Fischer-Tropsch process, it appears that there are decided advantages for the low-alpha case from the viewpoint of the Fischer-Tropsch reactor operation. The wax production rate is very low in this case and, assuming that the hydrocarbon products form ideal solutions and vapor, all Fischer-Tropsch products from an iron catalyst should leave the reactor in the vapor phase.[8] Even if this is not the case and some wax remains in the reactor, the wax fraction of the hydrocarbon products would be low. Because of the low rate of wax production, the amount of catalyst that must be removed in the liquid phase products would be a very small fraction of the reactor inventory. This, together with the demonstration of successful catalyst activation in an external unit by Sasol,[9] means that it should be no problem to activate a catalyst in syngas at one atmosphere. This activated catalyst could be added to the reactor as needed in order to maintain a constant catalyst activity and inventory in the reactor. In addition, it would not be necessary for the iron catalyst to be present in particles of 10 to 150 micron size as is needed for the high-alpha process where some filtration or gravity technique must be utilized for catalyst/wax separation in order to maintain a catalyst inventory in the reactor. This means that the fine 1-3 micron size particles would be acceptable, and would simplify catalyst preparation. In a commercial operation, it is inevitable that malfunctions of equipment will cause sudden interruptions of gas flow to the reactor. Settling of the catalyst once gas flow must be stopped would be much slower with the 1-3 micron particles than for the 10-150 micron catalyst particles so that preventing settling of the catalyst and redispersion of the catalyst during reactor restart should be much less of a problem with the small catalyst particles. Problems of catalyst settling and restarting a slurry reaction does not appear to have been a problem at the U.S. DOE's LaPorte faculty since gas flow has been routinely shut off to allow settling of the bed for the purpose of verifying the gas holdup. No problems were encountered in restarting the reactor after 15 minutes (10). However, other operators of slurry reactors indicate that restarting without loss of catalyst activity may be a problem unless special precautions are taken during shut down.

SUMMARY AND CONCLUSIONS

The performance of an iron-based catalyst for the Fischer-Tropsch synthesis has been analyzed for the purpose of increasing the hydrocarbon production rate. Syngas conversion rates are high at low conversion levels and continuously decrease at higher conversion levels. Further, a comparison of the relative reaction rates of the Fischer-Tropsch synthesis and the water gas shift reaction indicate that the fraction of CO converted to hydrocarbons is also higher at lower conversion levels. This indicates that it is beneficial from a hydrocarbon productivity standpoint to limit the syngas conversion in the reactor to a lower value. Higher overall syngas conversions can be achieved by either recycling the unconverted syngas back to the reactor or by having two or more reactors in series. The hydrocarbon space time yield is, for instance, doubled by using a recycle reactor with 67% syngas conversion per pass versus a single pass reactor operated at 90% syngas conversion.

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Figure 1. The conversion of CO (□), H_2 (△) on synthesis gas (H_2/CO = 0.7) (○) as a function of the inverse of the space velocity (270°C, 12.9 atm., 100 Fe/4.4 Si/0.71 K).

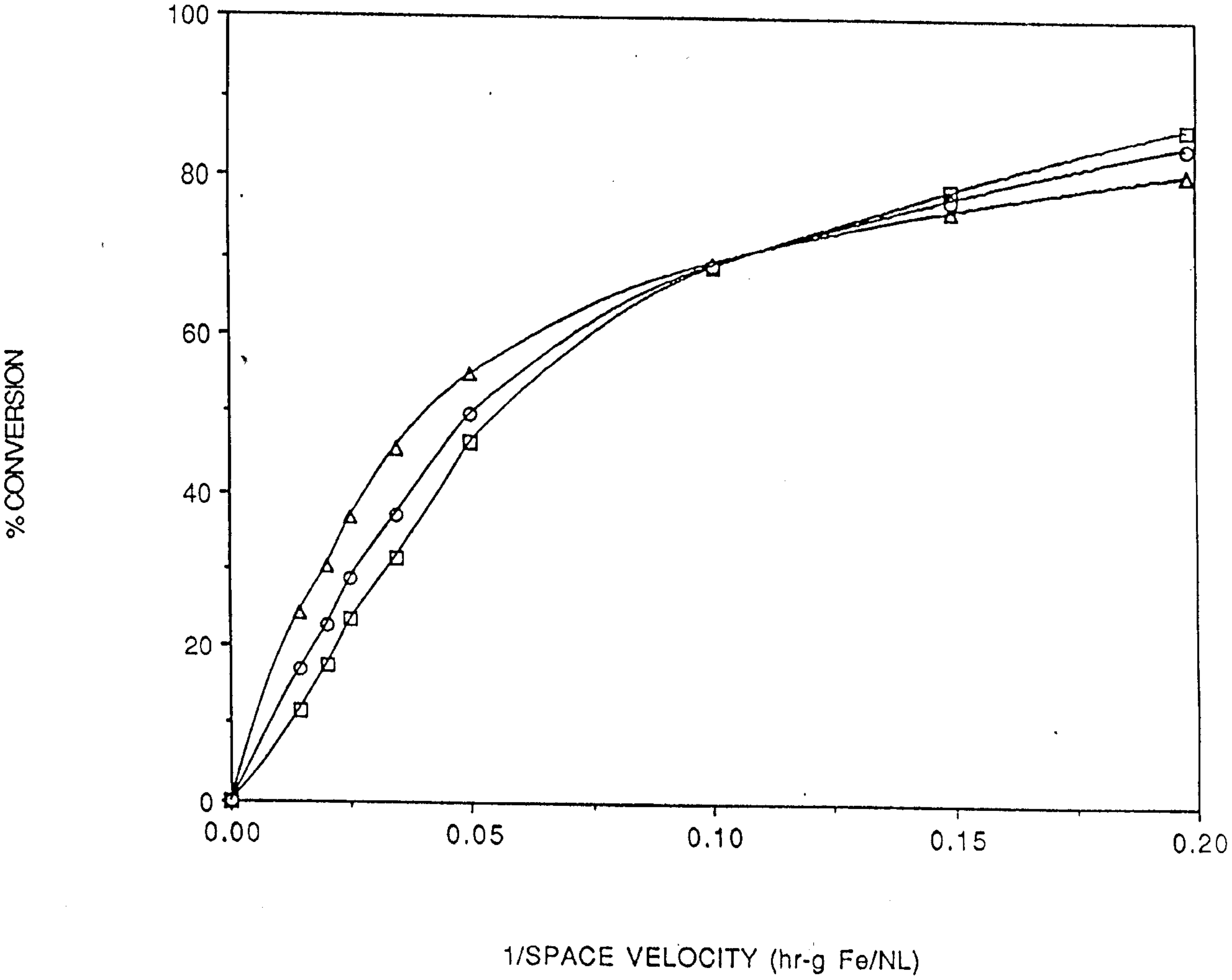


Figure 2. Relative rates for the formation of hydrocarbons (○, □) and the WGS reaction (△) with increasing CO conversion (100 Fe/4.4 Si/0.71 K, 270°C, 12.9 atm., $H_2/CO = 0.7$).

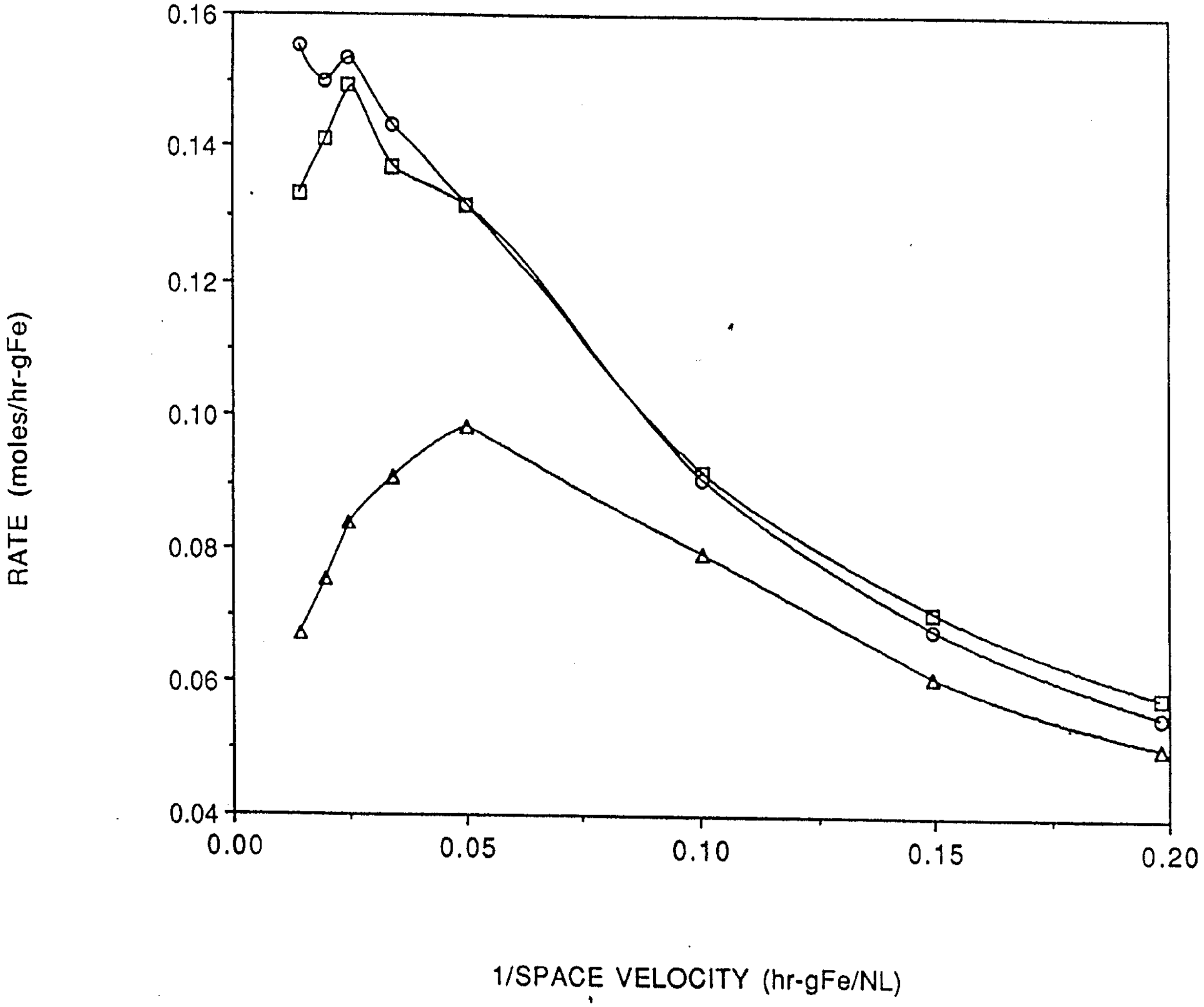


Figure 3. Fraction of CO producing hydrocarbons at increasing CO conversions ($270°C$, 12.9 atm., $H_2/CO = 0.7$).

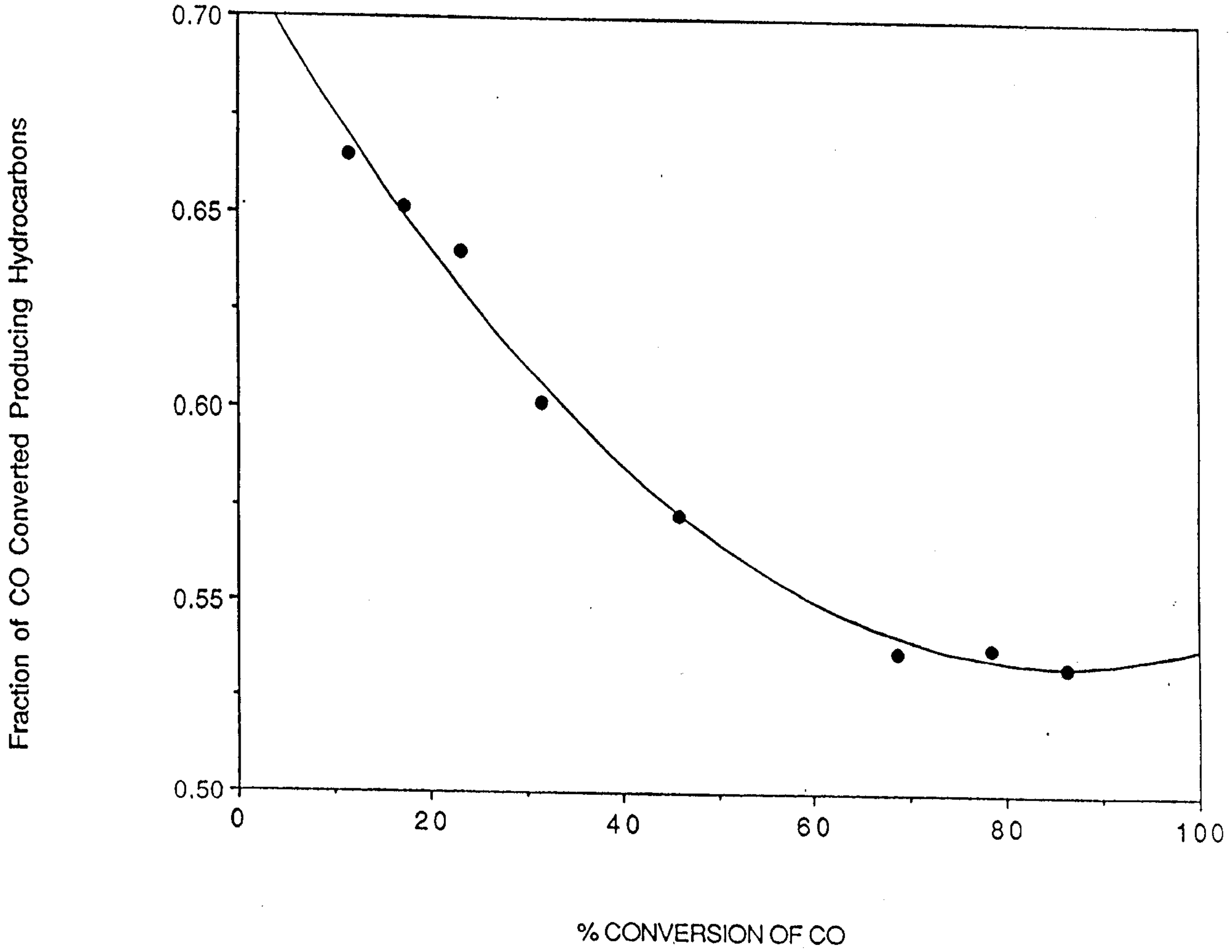


Figure 4. Grams of CO converted per unit reactor volume (100 Fe/4.4 Si/0.71 K, 270°C, 12.9 atm., $H_2/CO = 0.7$).

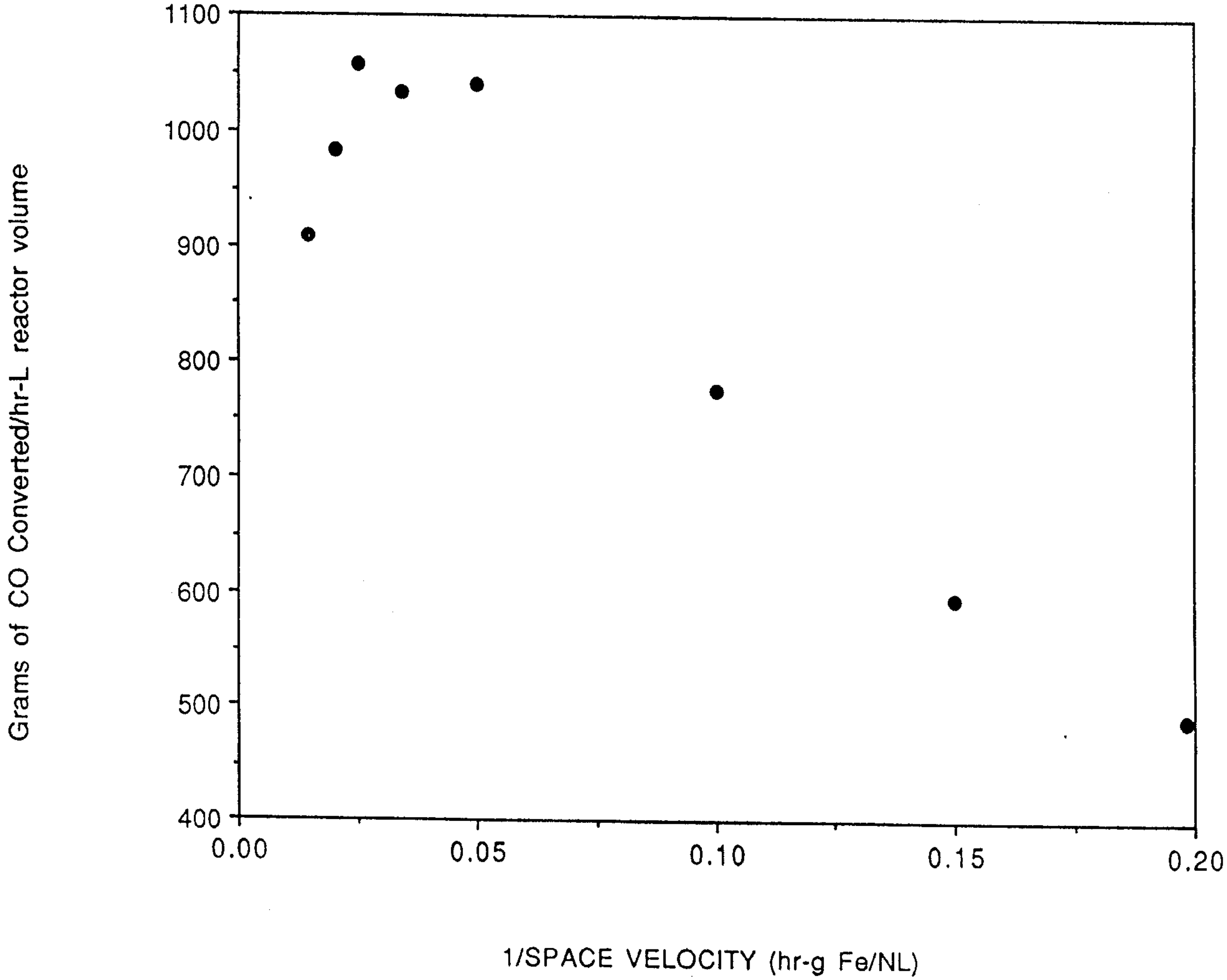


Figure 5. Grams of hydrocarbon produced per unit reactor volume (100 Fe/4.4 Si/0.71 K, 270°C, 12.9 atm., $H_2/CO = 0.7$).

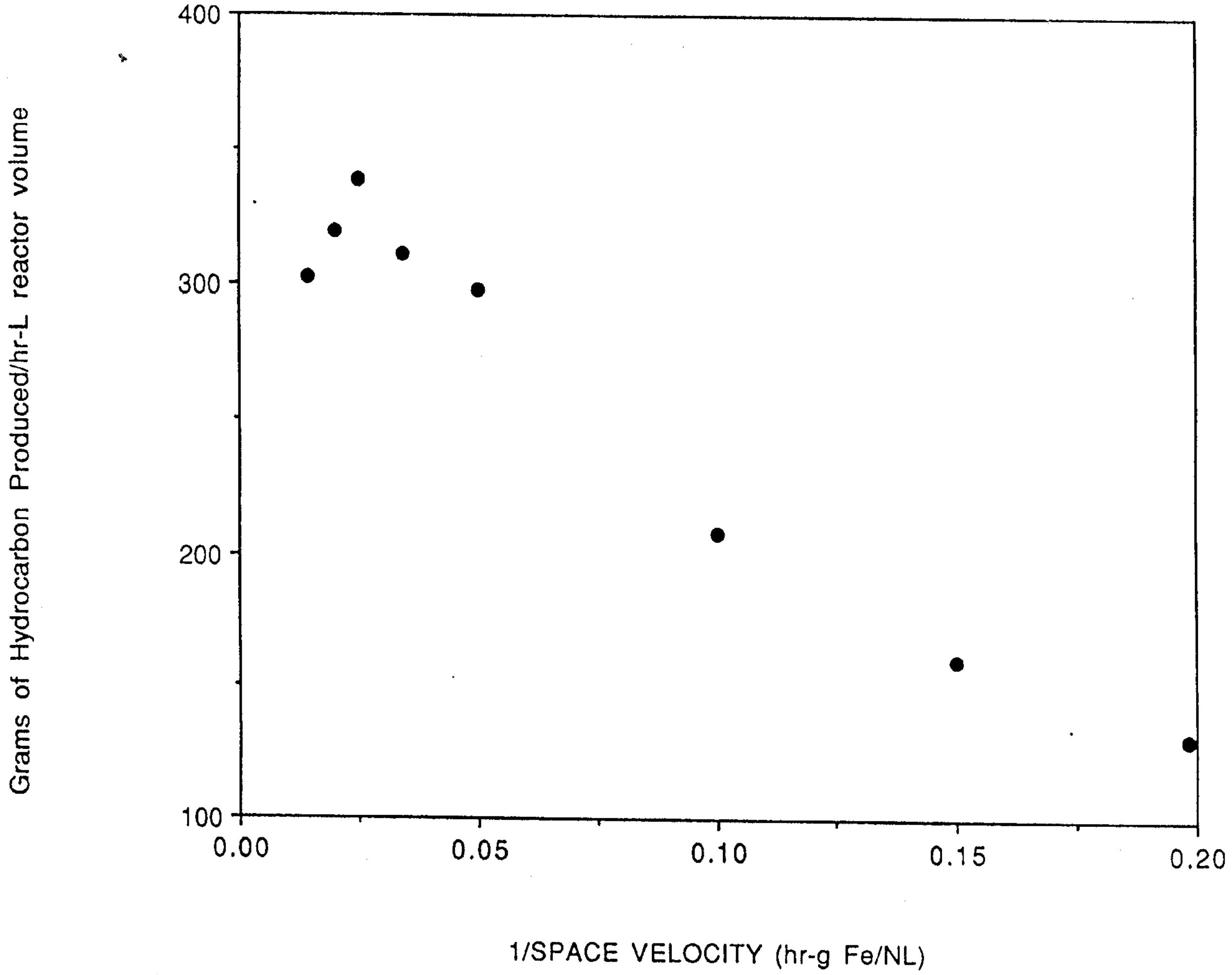


Figure 6. Grams of CO_2 produced per unit reactor volume (100 Fe/4.4 Si/0.71 K, 270°C, 12.9 atm., $H_2/CO = 0.7$).

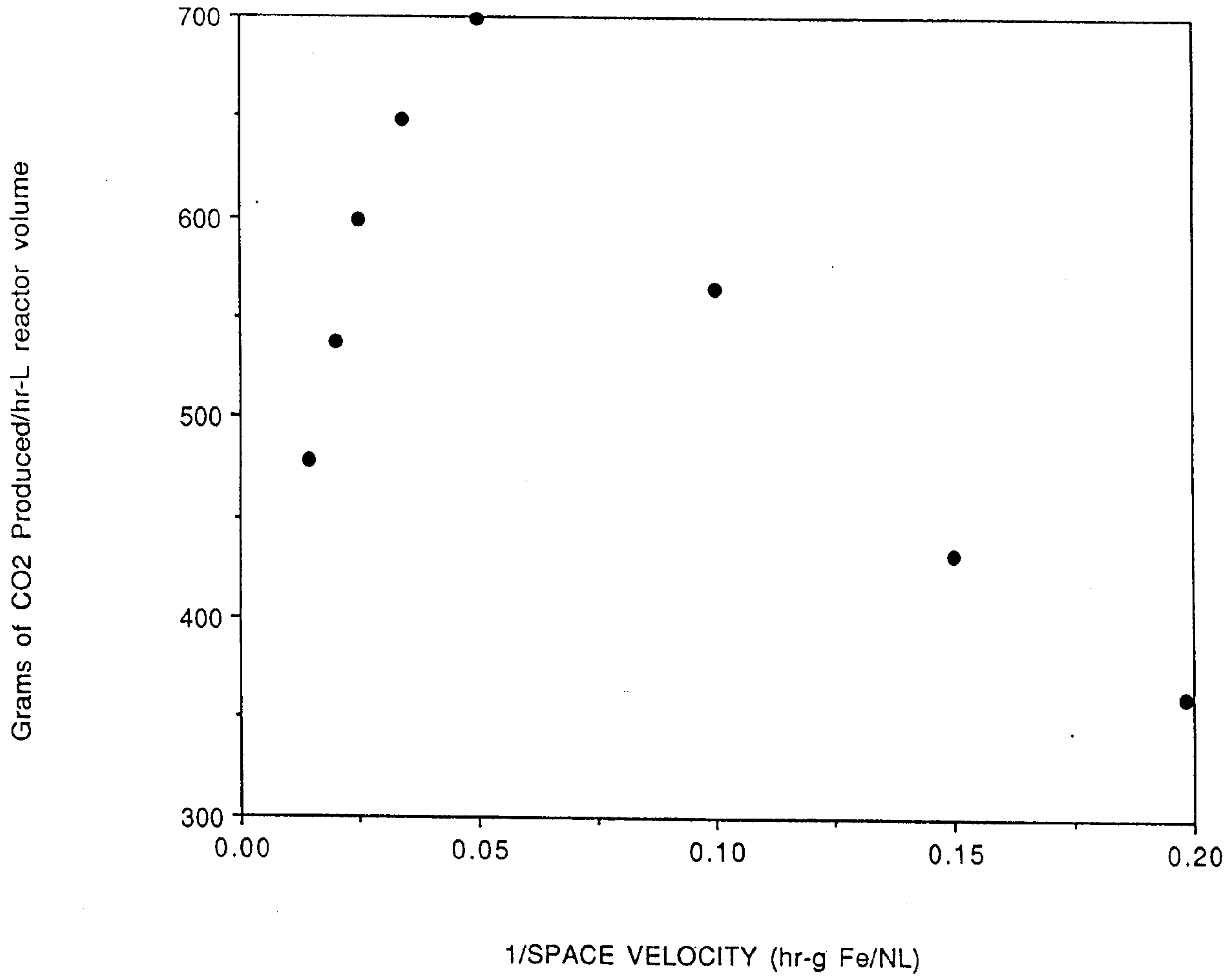
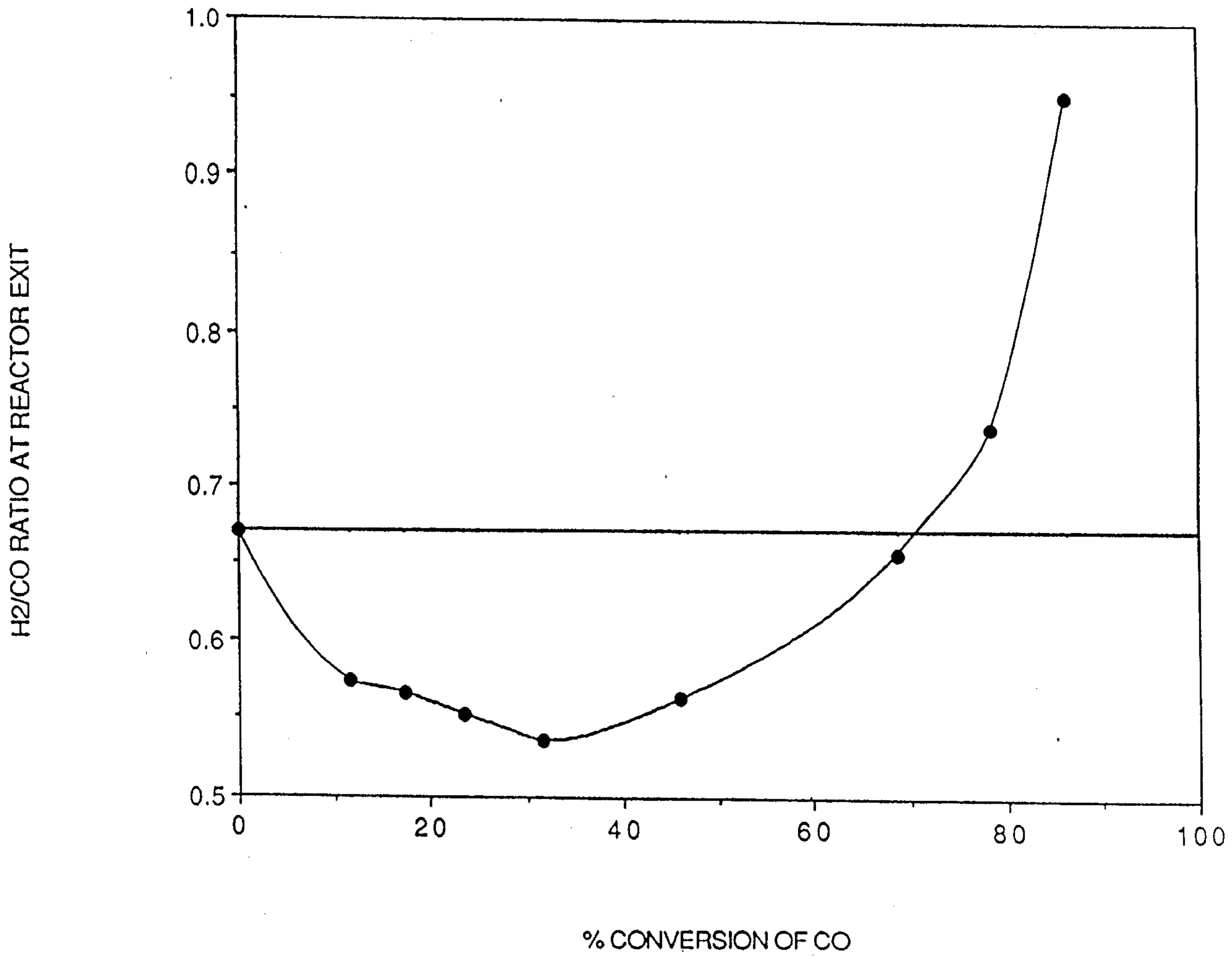


Figure 7. Exit H_2/CO ratio as a function of syngas conversion.



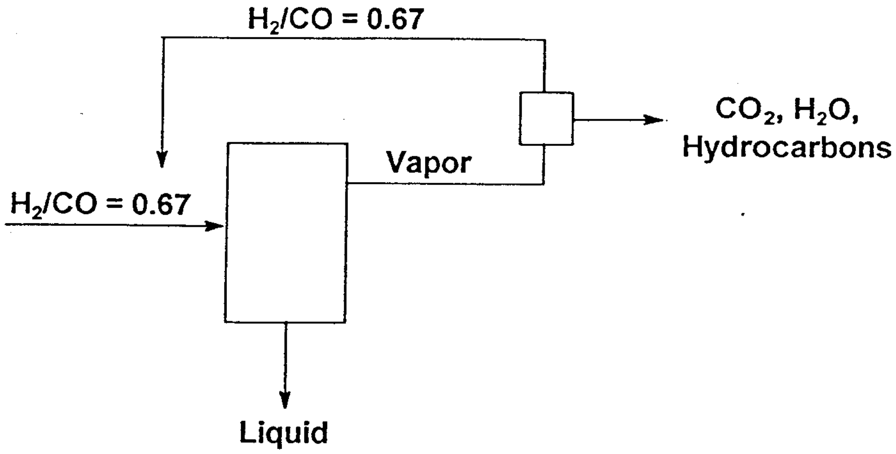


Figure 8. Schematic for recycle reactor which has same CO/H_2 ratio for the feed and exit gas.

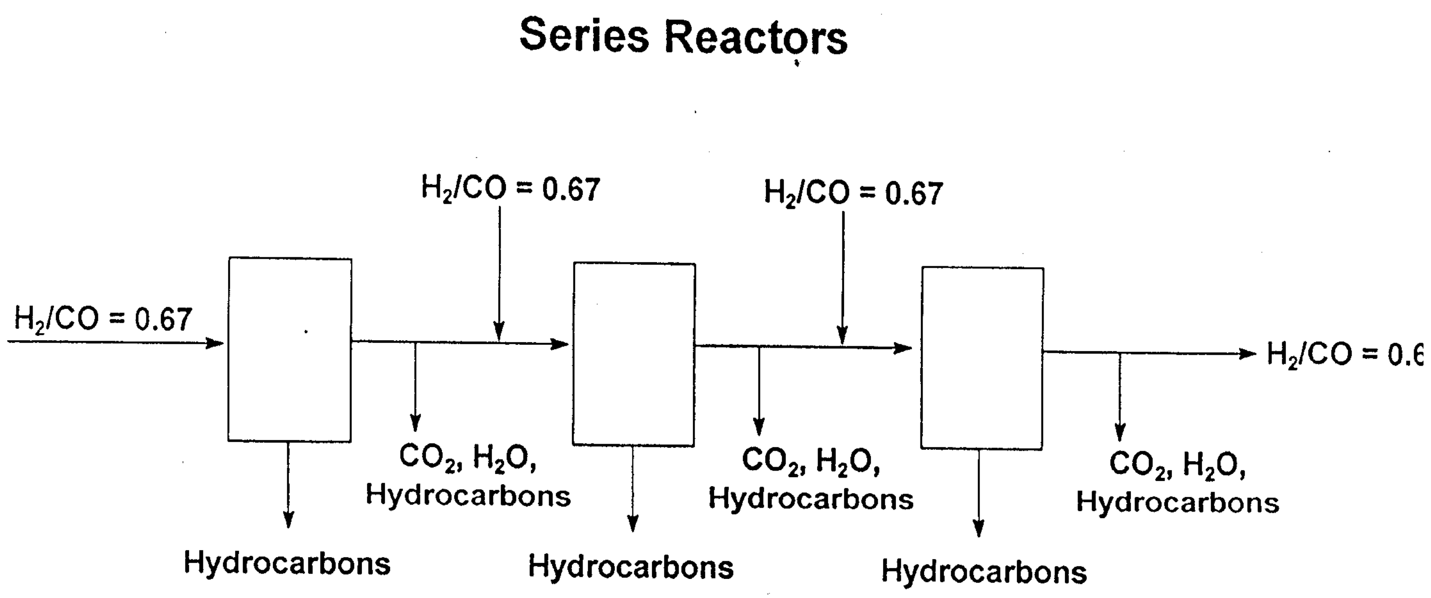


Figure 9. Schematic for use of the same sized reactors in series that are operated to have the same CO/H_2 ratio for the feed and exit gas.

Figure 10. Schematic of Fischer-Tropsch Synthesis with associated oligomerization and hydrocracking units.