

CHAPTER IX.H

PROCESS CONSIDERATIONS BASED ON CATALYST PERFORMANCE

A consideration of the conversions of CO and H₂ versus the flow rate for a syngas typical of the product from a modern coal gasification unit (H₂/CO = 0.7) shows that conversion rates of synthesis gas decrease with increasing CO conversions. For example, for the data shown in Figure IX.H-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, an operator pays a significant price in the reaction rate 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 IX.H-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 CO₂ and excess hydrogen at the higher CO conversion levels. Figure IX.H-3 obtained from the same data clearly shows that the lower CO conversion levels produce a higher fraction of hydrocarbons per unit CO conversion than for high CO conversion levels.

The above considerations imply that it is beneficial to operate the 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. 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 IX.H-1, the grams of CO converted per reactor volume are plotted in Figure IX.H-4 for increasing reaction times. It is seen that the rate decreases with reaction time with a maximum 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 IX.H-5. The production of CO₂ also decreases with reaction time (Figure IX.H-6) but the maximum occurs at intermediate values of reaction time (0.05 hr.-g(Fe)/NL). Thus based upon the reactor productivity of hydrocarbons, the syngas flow rate through the reactor should be high (40 NL/hr.-g(Fe)). This flow rate corresponds to a single pass CO conversion of 25%.

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 single reactor unconverted or to utilize some 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 single pass (or single reactor) CO conversion level. At the equivalence point (67% CO conversion) the unconverted syngas that exits the reactor has the same chemical composition as the syngas feed to the reactor. 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 excess hydrogen or carbon monoxide. Furthermore, the following discussion is based solely upon what should be the most efficient use of the catalyst. 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, CO₂ and H₂O from the vapor exiting the reactor prior to recycle of the unconverted syngas (Figure IX.H-7). The net result is, however, that recycle provides for essentially 100% conversion of the syngas (in contrast to 90% as in the contract target) and at an effective flow rate of syngas of 6.7NL/hr-g(Fe) rather than the targeted value of 3.4NL/hr-g(Fe). 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.

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 major disadvantage of not being able to interchange the reactors and of having to stock different replacement components for the two 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 IX.H-8).

The major objective of the present work must be the production of transportation fuels. 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 (IX.H-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 IX.H-9). 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, and the appropriate data yield are reproduced below (IX.H-2):

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	9.67
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 C₂-C₄ range for these products to be discarded; thus, these would be utilized to produce liquid transportation fuels, most likely using an oligomerization process. 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 and operation of a medium or high

pressure hydrocracking process would be considered to be as great, and probably greater, than that required for an oligomerization process. On the other hand, while some methane and ethane would be produced by the hydrocracking process, it is likely that the low- α process would produce more of these two gases than the high- α process.

For the U.S., gasoline is currently a dominant fraction of the transportation fuel market. The low α catalyst produces gasoline (65-75 wt.%) as the major product. Furthermore, Kölbl and co-workers (IX.H-3) 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 Kölbl and coworkers (IX.H-3) 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 α 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 α catalyst may be less than the expense of hydrocracking the heavy wax produced by the high α catalyst and the smaller fraction and poorer quality gasoline that is produced by the hydrocracking process.

For the Fischer-Tropsch process, it appears that there are decided advantages for the low- α 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. 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 (IX.H-4), 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 inventory in the reactor. In addition, it would not be necessary for the iron catalyst to be present in particles of 50 to 100 micron size as is needed for the high-alpha process where some filtration or gravity technique must be utilized for solid/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 50-100 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.

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.

REFERENCES

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- IX.H-2. V. U. S. Rao, G. J. Steigel, A. C. Bose, G. C. Cinquegrane and R. D. Srivastava, ACS, Div. Fuel Chem., **37**, 184 (1992).
- IX.H-3. H. Kölbl, P. Ackermann and Fr. Engelhardt, Erdöl Kohle, **9**, 225 (1956).
- IX.H-4. S. Africa ref on hydrogen regeneration.

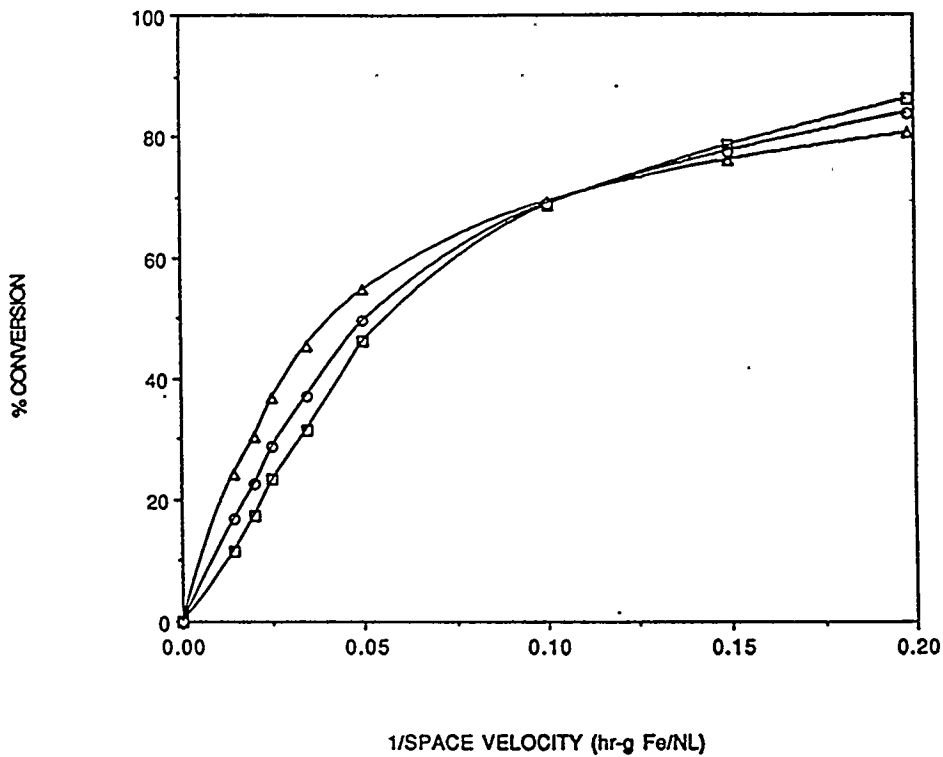


Figure IX.H-1. The conversion of CO (\square), H₂ (Δ) on synthesis gas (H₂/CO = 0.7) (\circ) as a function of the inverse of the space velocity (270°C, 12.9 atm., 100 Fe/4.4 Si/0.71 K).

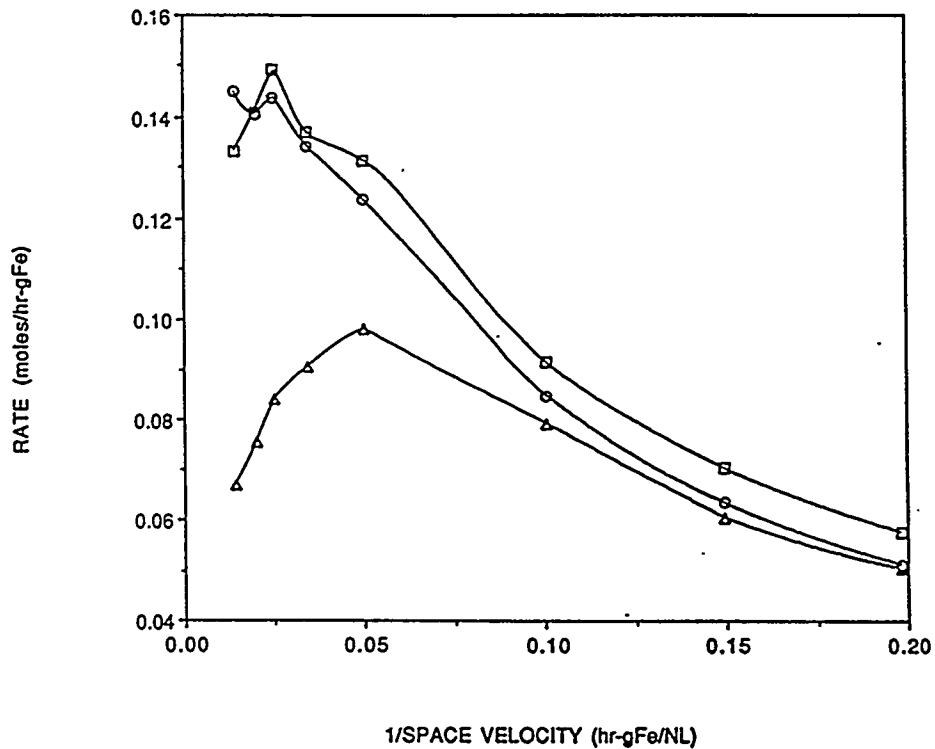


Figure IX.H-2. Relative rates for the formation of hydrocarbons (\circ , \square) and the WGS reaction (Δ) with increasing CO conversion (100 Fe/4.4 Si/0.71 K, 270°C, 12.9 atm., H₂/CO = 0.7).

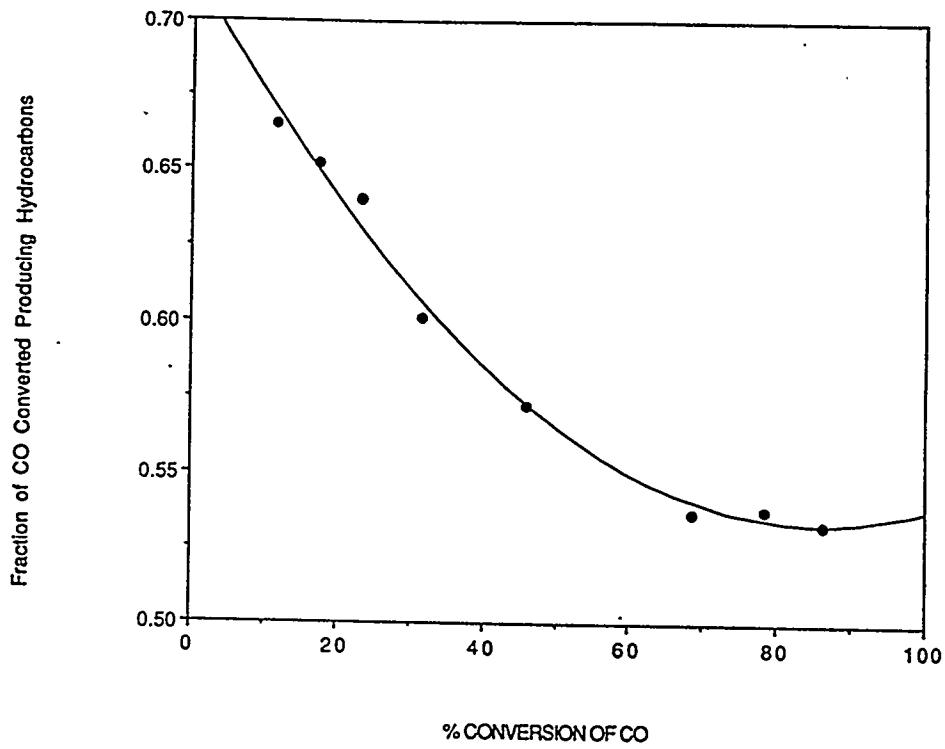


Figure IX.H-3. Fraction of CO producing hydrocarbons at increasing CO conversions (270°C, 12.9 atm., H₂/CO = 0.7).

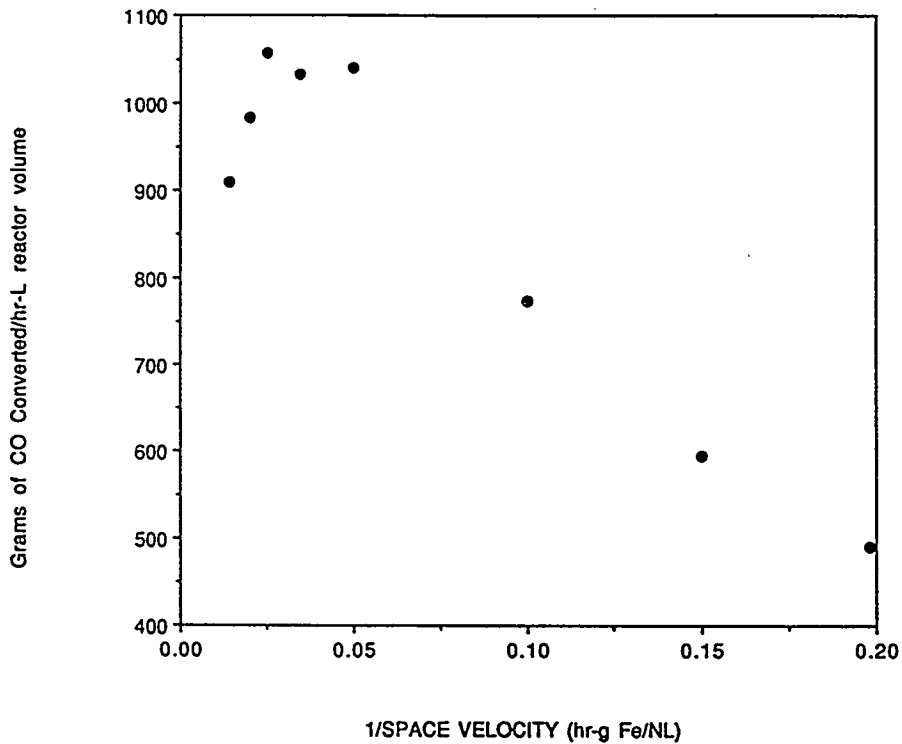


Figure IX.H-4. Grams of CO converted per unit reactor volume (100 Fe/4.4 Si/0.71 K, 270°C, 12.9 atm., H₂/CO = 0.7).

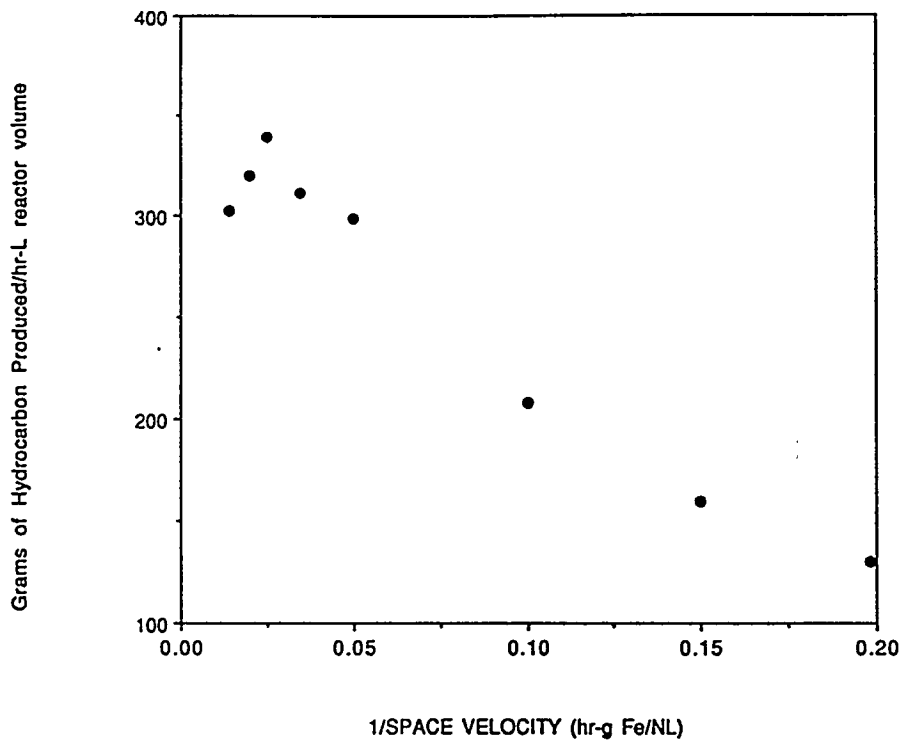


Figure IX.H-5. Grams of hydrocarbon produced per unit reactor volume (100 Fe/4.4 Si/0.71 K, 270°C, 12.9 atm., $H_2/CO = 0.7$).

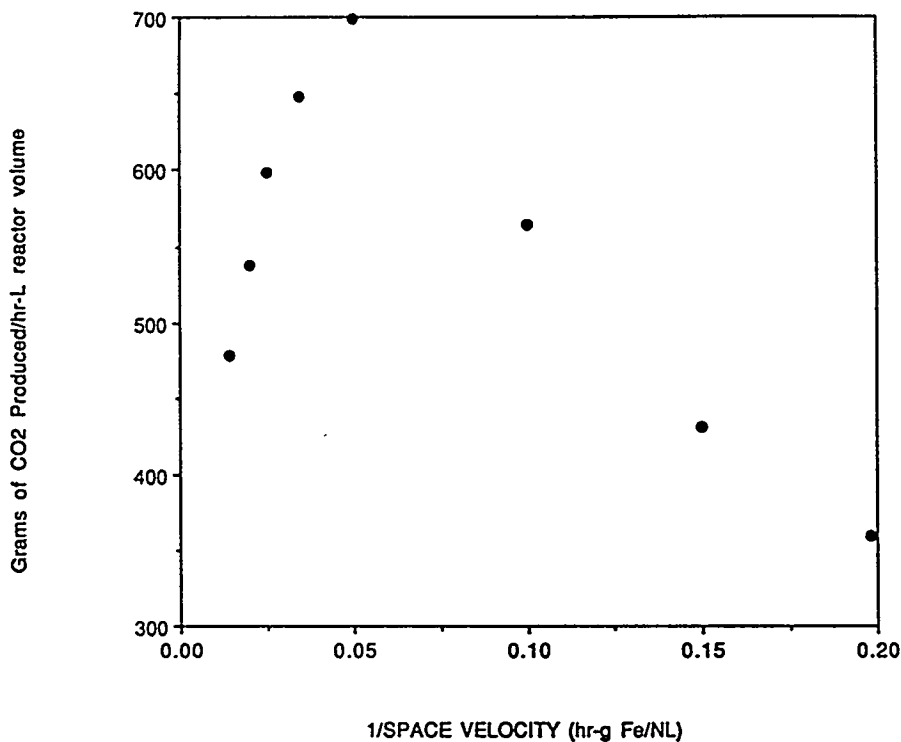


Figure IX.H-6. Grams of CO_2 converted per unit reactor volume (100 Fe/4.4 Si/0.71 K, 270°C, 12.9 atm., $H_2/CO = 0.7$).

Recycle

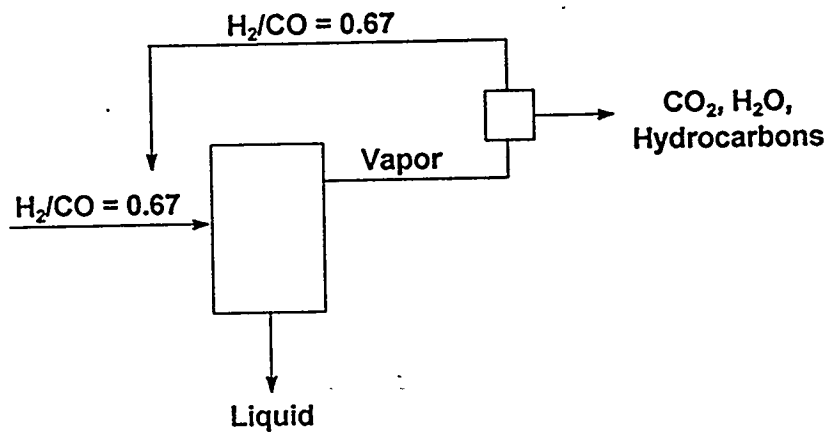


Figure IX.H-7. Schematic for recycle reactor which has same CO/H_2 ratio for the feed and exit gas.

Series Reactors

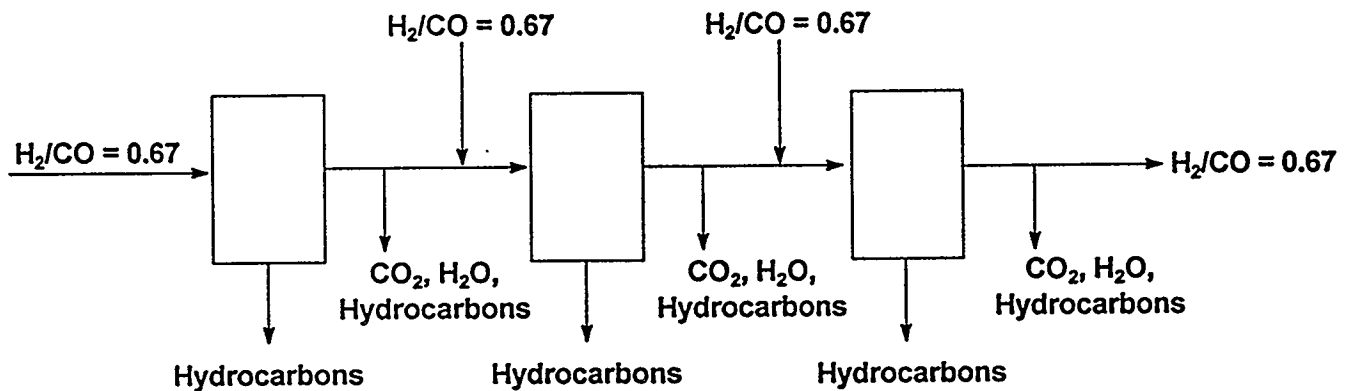


Figure IX.H-8. Schematic for use of the same sized reactors in series that are operated to have the same CO/H_2 ratio for the feed and exit gas.

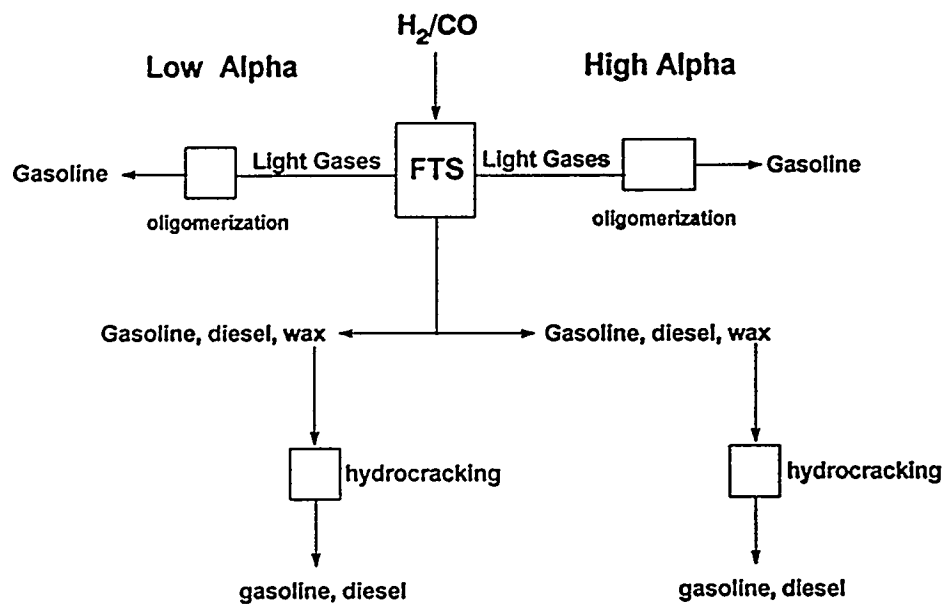


Figure IX.H-9. Schematic of Fischer-Tropsch Synthesis with associated oligomerization and hydrocracking units.