

In recent years, some FT technology developers have proposed the best path to an all liquid FT product is to use a low alpha FT catalyst in an attempt to eliminate the formation of wax molecules and therefore eliminate the need for a hydrocracking function. Others have proposed combining the FT reaction and the hydrocracking reaction all in the same reactor. Emerging Fuels Technology ("EFT") believes that the most cost effective approach, in terms of overall plant cost per barrel of marketable liquid produced, is through a very high alpha FT catalyst combined with hydrocracking/hydro-isomerization. This paper will explore "pros and cons" of these 3 options using publicly available data.

## First, an explanation of Alpha

The FT reaction is a polymerization of carbon monoxide and hydrogen with a distribution that can be described with a single polymerization constant commonly referred to as Anderson Schultz Flory alpha, or just "alpha" which satisfies the relationship

$$W_n/n = (1-\alpha)^2 \times \alpha^{(n-1)}$$

Alpha can be measured for any given FT catalyst and operating conditions by analyzing the liquid and waxy hydrocarbon product and plotting the log of the weight percent of each carbon number. The slope of the plot defines alpha. Alpha can be used to accurately predict the carbon distribution of the C3+ product. It is less accurate at predicting C2 and does not predict methane selectivity (production of methane). As a general rule methane selectivity goes up as alpha goes down.

Since the objective for most FT processes is to produce the most liquid hydrocarbon products with the least amount of capital it is desirable to optimize for maximum C5+ production. Light hydrocarbons in the C1-C4 range can be recycled or used as fuel in the process or both. However, recycle of any product has an associated cost as it requires additional capacity in the synthesis gas generation system and always results in some loss of carbon to CO2. The table below shows selectivity to different product fractions assuming a constant 10% methane selectivity with various alphas.

**Table A - alpha product yields (by Wt %) with methane fixed at 10%**

Alpha	C1	C2-C4	C5-C9	C10+	C24+
.75	10	29.25	37.32	23.43	.87
.8	10	20.38	33.89	35.23	3.1
.85	10	13.1	26.78	50.12	9.75
.9	10	6.5	16.58	66.92	26.59
.93	10	3.4	9.9	76.7	44.4

Note that the first 4 columns add to 100%. The last column demonstrates the percentage of total product made that is "waxy" based on alpha.

In reality, methane selectivity is not constant at 10% and in fact changes significantly with FT catalyst, reactor type and operating conditions. As a rule, methane goes up as alpha goes down. Table B is the same data as Table A but adjusted with an approximation of methane selectivity for a fixed bed reactor (based on EFT experience).

**Table B - alpha product yields (by Wt %) with variable methane selectivity**

Alpha	Recycled Products or fuel		Marketable Products		C24+
	C1	C2-C4	C5-C9	C10+	
.75	25	24.38	31.1	19.52	.72
.8	20	18.56	30.12	31.32	2.75
.85	15	12.37	25.3	47.33	9.21
.9	10	6.5	16.59	66.91	26.59
.93	6	3.56	10.33	80.11	46.38

Again, the first 4 columns add to 100%. The fifth column is the percentage of total product that is "waxy" (solid at room temperature). In most cases, only the C5+ products are marketable.

The FT reaction can use synthesis gas (CO+H<sub>2</sub>) from a large variety of synthesis gas generators which can use a broad range of feedstocks. Product strategy may change depending on plant location and incentives however, maximum product value will always be based on reducing the production of light gaseous products. Note: when the FT selectivity is optimum the BTU content of the tail gas often fits the energy requirement to drive the entire process so recycle is not needed. Process optimization based on recycle of off-spec/unsellable products often overlooks yield loss and the energy requirements for compression and other process drivers.

## The Low alpha/No Hydrocracker Approach

We chose USP# 9,896,626 issued to Greyrock Technology LLC as representative of a strategy based on low alpha product distribution to eliminate the hydrocracker. Table 2 in the patent describes a partial oxidation synthesis gas composition of H<sub>2</sub> 73%, CO 22% and CO<sub>2</sub> 5%. Assuming a final H<sub>2</sub>: CO ratio of 2:1 the adjusted synthesis gas would be H<sub>2</sub> 62%, CO 31% and CO<sub>2</sub> 7%. Using this synthesis gas feed and the tail gas analysis provided in Table 3 of the patent we calculated product selectivity as follows C1 29.8%, C2-C4 22.2% and C5+ 48%. This is close to the .75 alpha line in Table B above. The table shows that to virtually eliminate wax the FT alpha needs to be in this range.

The product carbon distribution demonstrates several problems with this strategy. First, total recoverable C5+ product is only about 50% of all hydrocarbons generated in the FT reactor. Second, of the total recoverable products, more than 60% is in the naphtha range, significantly less valuable than middle distillate products. Third, since 50% of the hydrocarbon product is C1 to C4, these light gases must be recycled back to the syngas generator to increase carbon efficiency, but at a cost. The synthesis gas generation system has to be substantially larger and more carbon is lost to CO<sub>2</sub> with each pass through the system. The synthesis gas generator's carbon efficiency is typically on the order of 85% (81.5% in the '626 patent example). If the FT reactor operates at 95% conversion with 50% selectivity to C5+ products the net carbon efficiency of any recycled product is no more than 40%. The reason to run the low alpha was to eliminate the cost of the hydrocracker. If we summarize the cost of the total plant as key unit operations the synthesis gas generation and clean up system will typically make up about 60 to 65% of the capex while the FT system will be about 20% and the hydrocracker/distillation will be at most 15 to 20%. Any light gas recycle increases the size and cost of the synthesis gas generation system and the FT system and does not eliminate the distillation column. The tradeoffs are not favorable and we believe any heads up analysis will show that low alpha FT operation will result in higher total installed cost, lower total yield and lower product quality per volume of product produced.

## Pros/Cons of Low alpha/No Hydrocracker Approach

Pros:

- Elimination of hydrocracker

Cons:

- Larger syngas generation equipment to handle recycle (approximately 50% larger, cancelling out the savings from elimination of the hydrocracker)
- Lower overall carbon efficiency (estimate 57% with recycle) negatively affecting Carbon Intensity score.
- More than 60% of marketable product in the naphtha range
- Diesel fraction does not have good cold flow characteristics due to high straight chain paraffin content

## The Combined FT/Hydrocracker Approach

Combining a FT catalyst and hydrocracking catalyst in one reactor is demonstrated in the patent literature in several patents issued to Chevron. We chose USP # 8,519,011 and 8,481,601 as representative of two variations of the method.

In USP #8,519,011 a strategy is disclosed to combine FT synthesis and hydrocracking as stacked zones in the same reactor. This is a challenging strategy for several reasons, first FT synthesis (low temperature non-shifting) is normally operated in a temperature range of 180 to 220 C whereas hydrocracking normally operates at 250 to 350 C. Therefore, it is necessary to utilize a hydrocracking catalyst that can work in the presence of substantial amounts of carbon monoxide and below the low end of the normal cracking temperature range. It also requires operating the FT catalyst at a high temperature typically seen at end of run (EOR) conditions. Normal FT reactor operation would be within a temperature range from start of run (SOR) to EOR. FT catalysts are constantly in a state of deactivation. Ideally the catalyst operates at a low deactivation rate and has a long operating time between SOR and EOR. This allows for the run cycle between regenerations to be long enough to fit within a normal plant maintenance cycle. Forcing the FT operation to start at EOR temperature does not provide for a long run cycle. Hydrocracking catalyst operating with a FT feed that has very low contaminant levels will operate at steady temperatures. Combining the two reactions in one reactor requires the operator to sacrifice optimum performance of both reactions. Short run cycles for the FT catalyst may result in the combined operations only working for short periods that produce mediocre data for a patent but are not practical for long term commercial operation.

In the '011 patent the maximum C5+ selectivity in Table 1 is 66% and this is mostly naphtha. The CO conversion for this data point is only 22.5% so it is not representative of commercial operation. The stacked bed has 150 mg of FT catalyst and 189 mg of hydrocracking catalyst. (In an EFT design where the two unit operations are optimized separately the hydrocracking catalyst volume is about 20% of the FT catalyst volume.) The FT reactor is significantly more expensive than the hydrocracker so using a large portion of the FT reactor volume for hydrocracking catalyst has a cost for increased volume and an added cost for

more cracking catalyst. An optimized FT reactor can produce approximately 90% C5+ and after cracking the product has a high yield of the more desirable distillate fraction. As expected the combined operation results in sacrificed yield and quality of product and the added catalyst volume and reactor cost offsets most if not all cost savings for eliminating the hydrocracker and related components around the hydrocracker.

The '601 patent shows results of a physical mix of FT catalyst and cracking catalyst. The net C5+ selectivity is 84% with only 4% C21+ (wax). This is significantly better than the C5+ selectivity of the '011 patent but not as good as the best operation demonstrated by EFT with 90% C5+ selectivity in the FT reactor. The FT catalyst in the '601 patent contains 5% Ruthenium which we estimate will make the catalyst cost approximately 5x what the EFT FT catalyst costs. FT catalysts are expensive and the cost must be amortized over the life of the catalyst. EFT has spent years on activation and regeneration methods (notice of allowance for new patent received July 11, 2019) to maximize the useful life of our FT catalyst. With a three year life the amortized FT catalyst cost is approximately \$3/Bbl. If as expected we are able to ultimately demonstrate useful life of 5 years, the amortized cost will drop to about \$2/Bbl. This is an important number which we believe to be industry best. Table 2 and 3 of the '601 patent shows long term aging data indicating a high deactivation rate. We highly suspect that the amortized cost of the FT catalyst is an order of magnitude higher than EFT's FT catalyst making the FT/hydrocracking system described in the '601 patent non-commercial.

Systems and methods are described in these patents to produce FT products with little or no wax. We submit that the penalties (high cost, low yield and poor product quality) far outweigh any benefit associated with elimination of the hydrocracker. We note that it is not total elimination as a distillation column is still required in all cases and in small remote locations the distillation column may be the most difficult part of the hydrocracker system to operate.

## Pros/Cons of Combined FT/Hydrocracker Approach

Pros:

- Eliminate some hydrocracking components

Cons:

- Higher FT catalyst cost (5x higher)
- Shorter cycles between FT regenerations due to high starting temperature, less uptime
- Higher hydrocracking catalyst cost (larger volumes)
- High naphtha yields - approximately 44%

## EFT's Approach (High alpha with Hydrocracker)

Emerging Fuels Technology (EFT) designed its proprietary FT catalyst with the objective of maximizing alpha and minimizing methane selectivity for all syngas sources and feedstocks. The EFT process and FT reactor design has also been driven with this common goal. Maximum distillate yield or maximum lube base stock yield both come from this case. EFT has achieved an alpha as high as .93 on a consistent basis. With

a .93 alpha and proper hydrocracking diesel yields can exceed 80% with little or no recycle of FT hydrocarbon products back to syngas generation. (With hydro-isomerization, lube base stock yield can exceed 40%)

EFT has tested several non-noble metal and noble metal cracking/isom catalysts prior to developing an upgrading design. Table C shows the typical results.

**Table C - High alpha product yields (by Wt %) with Hydrocracking Results**

Alpha	Recycled Products or fuel		Marketable Products		
	C1	C2-C4	C5-C9	C10+	C24+
.93	6	3.56	10.33	80.11	46.38
			(naphtha)	(diesel) C10-23	
Hydrocracked			18-20	80-82	0.0

## Pros/Cons of High alpha/Hydrocracker Approach

Pros:

- .93 alpha FT catalyst generates 90% selectivity to C5+ products
- Higher carbon efficiency - 68% (more barrels made per unit of gas processed)
- Smaller Syngas Generator required - little or no recycle
- Higher yield of middle distillates - 80%+ (after hydrocracking)
- Higher quality middle distillates, control of final properties
- Low naphtha yield - less than 20% (least valuable product)
- Option to make specialties - lube base stocks

Cons:

- None

EFT has also developed a method to remove the most expensive parts of a hydrocracker system. With this modified method we believe the hydrocracker capex will be less than 10% of the total plant capex with no loss of yield or quality. Combined with the high selectivity to C5+ products and high yield of finished distillate products we believe the conservative approach that separates and optimizes both FT and hydrocracking will always show superior economics, better products and better operability.

## Summary

In Table D below we have summarized percentages of marketable products from each method along with the overall product yields from each method based on an input of 10,000 scf of natural gas feedstock.

**Table D - Product yields per 10,000 scf of natural gas for each Method**

Method	Marketable Products (% of barrel normalized)		BBLs per 10k scf	Estimated Carbon Efficiency	Estimated Thermal Efficiency
	Naphtha	Diesel			
Low alpha, no HC	60-65	35-40	.8	54%	44%
Combined FT/HC one reactor	46	54	.9	63%	51%
High alpha w/ separate HC	18-20	80-82	.95	67%	55%

This clearly demonstrates another significant advantage of EFT’s approach. The total marketable products produced are almost 19% more (.8/.95 = 1.1875) than the total products produced from the low alpha approach in addition to being more valuable because of the higher diesel yield.

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About Us:

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