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FISCHER-TROPSCH PRODUCTS AS LIQUID FUELS OR CHEMICALS
An Economic Evaluation

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Fischer-Tropsch synthesis, petroleum refinery, chemical properties of Fischer-Tropsch products, physical properties of Fischer-Tropsch products, economic evaluation, FT products as liquid fuels, FT products as chemicals.

The compatibility between the Fischer-Tropsch Synthesis (FT) and the economic role of the petroleum refining industry is examined. The economic advantage of the FT synthesis utilized within a petroleum refinery is explored. Also examined are the chemical and physical properties of the FT products. Although the FT distillate fuels have exceptional properties, FT naphta is difficult to reform into gasoline. The refiner may choose to utilize lighter FT products in petrochemical applications when FT is viewed as a supplement, rather than an alternative to petroleum refining.

1. Introduction

This paper examines the compatibility between Fischer-Tropsch synthesis (FT), and the petroleum refining industry's economic role. We begin with the traditional view of a stand-alone refinery, then expand the view to include raw-material supply and refined-product markets. Rather than looking at FT as a stand-alone alternative to a petroleum refinery, we choose to look at FT synthesis utilized within a petroleum refinery.

We also examine the chemical and physical properties of FT products. FT distillate fuels have exceptional properties, however FT naphtha is difficult to reform into gasoline. The refiner may choose to utilize lighter FT products in petrochemical applications. This option becomes more attractive when FT is viewed as a supplement, rather than an alternative to petroleum refining.

A STANDARD VIEW OF THE REFINER'S ECONOMIC ROLE

Fig. 1 depicts a standard view of the refiner's economic role. Crude oil is the input, the refiner defines the transformation process, and the output is a slate of

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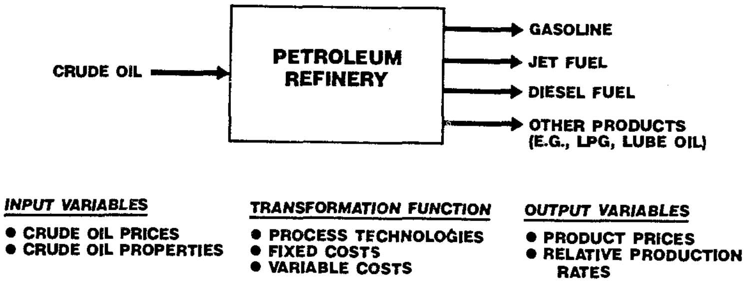


Fig. 1. Standard view of refiner's economic role.

finished products. Refiners construct linear programs with similar boundaries in optimization and planning studies. Sensitivity and "what-if" analyses are easily handled. This model helps to explain why the most flexible refinery is often the most profitable refinery, because we can adjust the transformation function for simultaneous input and output variations.

One limitation in the standard view arises from not recognizing refinery products as intermediates, utilized in downstream consumer markets. Using gasoline as an example, the downstrem market involves the general public, governments, automobile manufacturers, and refiners (fig. 2). The output is an automobile-based transportation system. The degree of individual mobility provided by this transportation system is an integral part of our society, which explains governmental participation in the process. Clearly, any factors that change the environment of the downstream market can dramatically impact the refiner.

A second limitation of the standard view is that it does not consider multiple or alternative inputs to the refinery. Crude oil is the sole feedstock, and crude oil prices and compositions are the input variables. There is only a finite quantity of crude oil available for production. Eventually, the price of oil will rise relative to other fossil fuels that are found in relatively greater abundance. This trend will

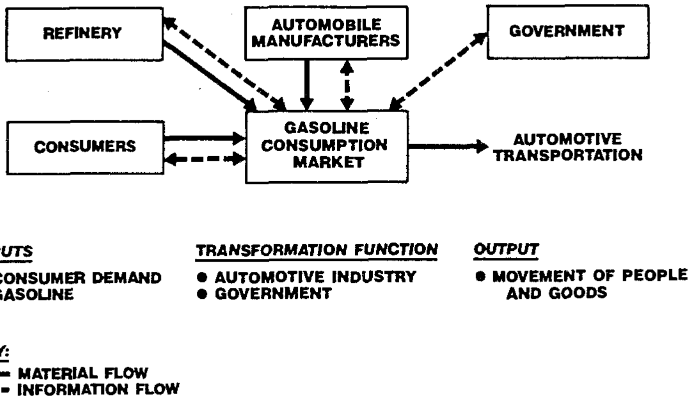


Fig. 2. Gasoline market interactions.

erode the economic advantage of crude oil as the sole feedstock to a refinery, and spur consideration of supplements or alternatives.

AN EXPANDED VIEW OF THE REFINER'S ECONOMIC ROLE

Fig. 3 depicts an expanded view of the refiner's role. This view considers multiple input options. On the output side, we include the downstream environments of key-intermediate products. The main advantage of the expanded view is the ability to link input, output, and refinery-configuration decisions to the dynamics of the product markets. This is particularly important for Fischer-Tropsch because both the feed source and intermediate product compositions are substantially different from traditional petroleum refining. Within the standard view, the refining industry reacts to new product demands and specifications determined externally. The expanded view may be more realistic. Each major participant is pro-active, attempting to either maintain or change the existing market equilibrium. Recent events in automobile and diesel fuel markets are a good example. All participants bring viewpoints, information, and political pressure into a debate. What should we do, or not do, to fuel compositions to achieve cleaner air? Just as it is important for refiners to participate in the debate, it is also essential to consider the possible outcomes, and plan accordingly.

Direct and indirect methane-conversion research fit into the expanded view of refining. Instead of viewing methane as fuel for fired heaters, refiners are pursuing technologies to utilize methane as an additional feedstock to a refinery. In the area of FT, Shell and Statoil are at different stages of commercializing technologies to utilize remote natural gas [1,2]. Each refiner undoubtedly analyzed the situation in a broad context. Technology, product slate, government regulations and incentives, and finance are all important considerations. Also, there needs to be consistency between the project and the existing resources and strategic plans of the organization.

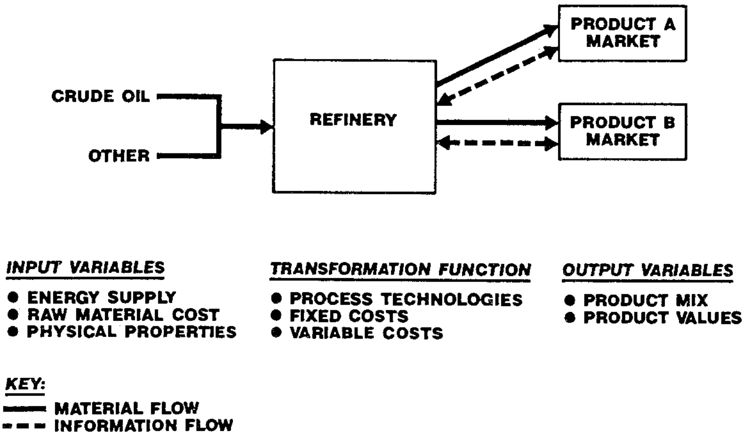


Fig. 3. Expanded view of refiner's economic role.

2. FT products as liquid fuels

The two commercial developments cited above share a common emphasis on diesel and jet fuels. If the intent is to produce liquid fuels, there are at least three good reasons for a distillate emphasis. We will list these reasons, then discuss each in more detail.

1. The chain-growth mechanism of FT is not selective to a specific boiling-range product. A high chain-growth probability maximizes wax formation, and FT wax can be selectively hydrocracked to distillates. The net effect is a high overall yield of middle-distillate products.
2. FT derived jet and diesel fuels have unique and valuable product attributes.
3. Middle-distillate production is less complex and less capital intensive than gasoline production from a FT derived feedstock.

HIGH MIDDLE DISTILLATE YIELDS

The Schulz-Flory polymerization law describes the probability of step-wise chain growth of hydrocarbons, independent of carbon number. The chain-growth probability is a fundamental property of any FT catalyst, and influences the overall product distribution. The careful choice of FT catalyst and process operating conditions determines the overall product distribution. Regardless of these choices, FT produces a wide molecular-weight range of products.

Degree of polymerization is defined as:

$$DP = 1/(1-p) \text{ where } p = \text{chain growth probability.} \qquad (1)$$

As chain growth probability increases from 50% to a 95%, the degree of polymerization increases from 2 to 20. The weight fraction for a specific carbon number is defined as:

$$Wn = n\left(p^{(n-1)}\right)(1-p)^2 \qquad (2)$$

where
Wn = weight fraction of carbon number n
n = carbon number, and
p = chain growth probability.

Eqs. (1) and (2) are used to depict the relationship between the degree of polymerization and the mass fraction of various product ranges (fig. 4). If you choose to maximize naphtha for gasoline production, there is a substantial penalty in light ends formation (about 35 wt% of the FT product). If instead, you choose to maximize straight-run distillate, the maximum achievable weight fraction of primary product is less than the maximum naphtha case, but the light ends production is cut by more than a factor of three.

There is further incentive to increase the degree of polymerization. UOP completed a DOE-sponsored study of FT wax hydrocracking in 1988 [3]. This

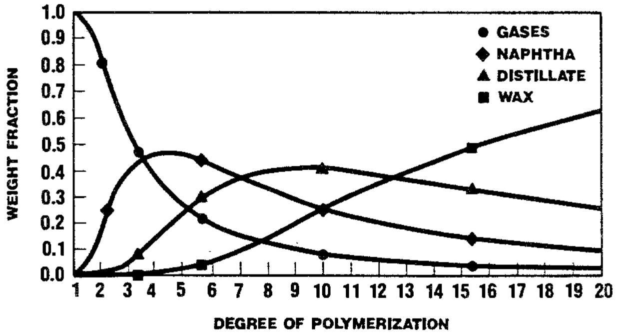


Fig. 4. FT product distributions.

study demonstrated that FT wax can be hydrocracked to distillate products at high yield (table 1). If you account for hydrocracked product, the overall yield of distillate steadily increases with the degree of polymerization (fig. 5). We adjusted the weight fractions plotted in fig. 5 for the hydrocracker yields in table 1. If the goal is maximum distillate production, the incentive to increase the degree of polymerization is evident because by-product yields are minimized.

Table 1
FT wax hydrocracking results

Arge FT wax feedstock	
Average Carbon No.	43
API, deg.	22.3
Paraffins, wt%	88.0
Olefins, wt%	5.7
Aromatics, wt%	0.3
Oxygenates, wt%	6.0
Branched molecules, %	2.3
HC process conditions	
Pressure, kPA (psig)	6,895 (1,000)
LHSV, 1/hr	1.0
CFR	1.5
Recycle H_2, SCMB (SCFB)	282.6 (10,000)
Conversion to 371° C,%	100
H_2 consumed, SCMB (SCFB)	14.6 (518)
*Product yields, wt-% **	
C_6 –	8.1
C_7 to 148° C (Naphtha)	10.0
149° C to 288° C (Kerosine)	34.0
289° C to 371° C (Mid. Dist.)	48.1

* Yields on fresh feed basis. Yields will sum to greater than 100% due to H_2 addition.

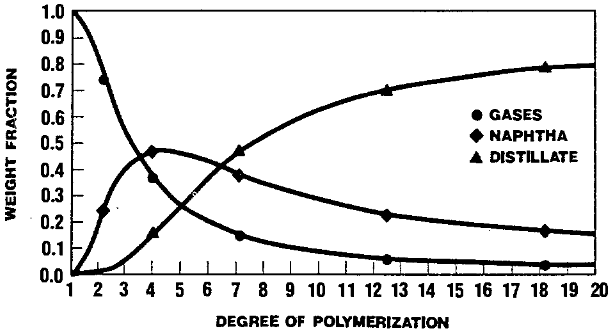


Fig. 5. Inclusion of wax hydrocracking.

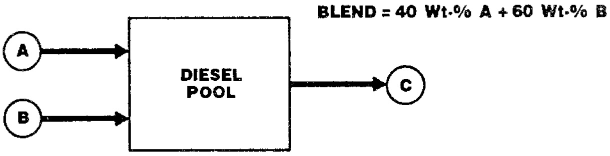
VALUABLE ATTRIBUTES OF FT DISTILLATES

Distillate products made via FT have desirable properties. Table 2 describes jet and diesel fuel properties produced in the UOP FT wax hydrocracking study. The jet fuel's smoke point and the diesel fuel's cetane number are exceptionally high. The FT products have no sulfur, no nitrogen, and no aromatics. They may be the most environmentally acceptable hydrocarbon turbine and diesel fuels that can be made.

A refiner could utilize the desirable FT distillate properties in at least three ways. Using diesel fuel as an example, the blending value of the FT distillate product is illustrated in fig. 6. A low-value, high-aromatic material such as light cycle oil (LCO) can be blended into the diesel pool without dropping the pool below 40 cetane, the 2-D diesel minimum. In this example, the FT distillate has an 87 \$/MT premium value as a blending agent. If you use 40 \$/MT as a conservative estimate of the blending value, this still represents a 21% increase in

Table 2
Hydrocracked product properties

Product	Arabian		
	Arge	VGO	Specifications
1149 °C–288 °C			*JET A*
API	54.2	41.7	37–51
Aromatics, vol%	0.0	16.7	–
Smoke point, mm	> 50	10.7	25 min.
Flash point, °C	47	39	38 min.
Freeze point, °C	−43	< −50	−40 max.
289 °C–371 °C			*2-D Diesel*
API	44.9	37.1	–
Cetane number	> 74	65	40 min.
Flash point, °C	163	163	52 min.
Pour point, °C	−7	−18	−7 max.



A = F-T DISTILLATE	B = LIGHT CYCLE OIL (LCO)	BLENDED PRODUCT
• STREAM VALUE = ?	• STREAM VALUE 19.32 $/bbl 128 $/MT	• API = 30.2° • ASTM 50% POINT = 283°C • CETANE NO. = 45 • FLASH POINT = 84°C • POUR POINT = -18°C • PRODUCT VALUE 24.51 $/bbl 186 $/MT

0.4 (x $/MT) + 0.6 (128 $/MT) = 1.0 (186 $/MT)
x = 273 $/MT

BLENDING VALUE OF F-T DISTILLATE = 273 $/MT-186 $/MT
= 87 $/MT OVER DIESEL VALUE

Fig. 6. Value added to LCO by blending with FT distillate.

the value of the FT distillate relative to diesel fuel. If the refiner chooses not to blend, the FT diesel will achieve a premium price in the market place, if consumers perceive it as a higher-value product. Finally, the desirable environmental features of this fuel may benefit the refiner's position, with respect to the downstream equilibrium between market participants. The benefit could be reducing the likelihood of governmental intervention, or perhaps increasing the market share for diesel engines, redesigned to take advantage of these unique fuel properties.

UPGRADING TECHNOLOGIES TO PRODUCE GASOLINE AND DISTILLATE FUELS

A hydrocracker is the only catalytic process needed to convert heavy FT reactor products into distillate fuels (fig. 7). FT wax is an ideal feed to hydrocrack because it is extremely paraffinic. An FT wax hydrocracker operates at less than

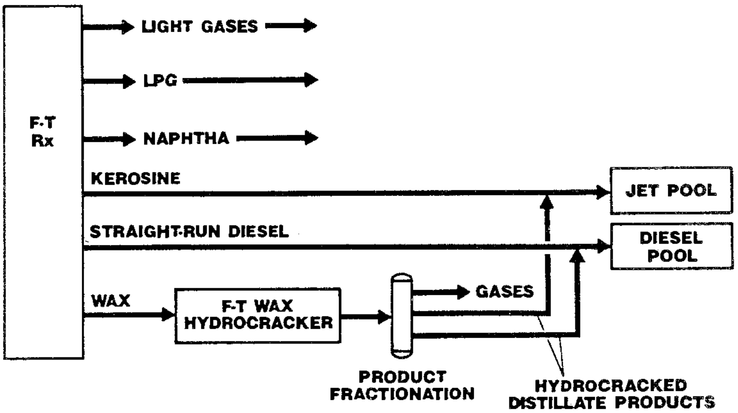


Fig. 7. Distillate production with FT wax hydrocracker.

half the pressure, twice the space velocity, requires about one-third the hydrogen, and displays better catalytic stability compared to hydrocracking petroleum vacuum gas oil (VGO). A FT wax hydrocracker has a lower estimated erected cost (EEC) than a petroleum VGO hydrocracker, primarily due to the lower pressure, higher space velocity operation.

It is easier to convert FT wax into distillate fuels than to convert FT naphtha into gasoline. A typical petroleum refinery converts raw naphtha into gasoline using two catalytic processes in series, hydrotreating and reforming. SASOL uses the same sequence to upgrade FT naphtha into high-octane gasoline [4]. Raw FT naphtha is more olefinic, has fewer ring compounds (naphthenes and aromatics), and has more oxygenates than a petroleum naphtha. Removal of sulfur and nitrogen compounds is of primary importance with petroleum naphthas, whereas FT naphtha is virtually sulfur and nitrogen free.

Despite the absence of sulfur and nitrogen, hydrotreating FT naphtha is still challenging. Oxygenates and olefins deactivate reforming catalyst, so they must be removed by the hydrotreater. Oxygenate removal requires temperatures and pressures that would polymerize olefins and rapidly coke-up the hydrotreating catalyst. Therefore, the hydrotreater design must accommodate the saturation of olefins at low temperature and then convert oxygenates at higher temperature, after the olefin content is reduced. The hydrotreated FT naphtha is even more paraffinic than the raw naphtha because olefins and oxygenates are converted to paraffins.

The paraffinic nature of FT products is an advantage for the hydrocracker, but a disadvantage for the reformer. Table 3 compares two hydrotreated petroleum naphthas and two hydrotreated FT naphthas [5]. Reformers are designed to maximize aromatics yield, and this objective becomes increasingly difficult as the paraffinicity of the naphtha increases. The lean naphtha by petroleum standards is a rich naphtha by FT standards. Compared to traditional reforming pressure (860 kPa or greater), low pressure reforming (345 kPa) can greatly increase the liquid product yield for a paraffinic feedstock [6]. However, the fact remains that

Table 3
Comparison of hydrotreated naphthas

	Rich petroleum naphtha	Lean petroleum naphtha	Synthol FT naphtha	Arge FT naphtha
Paraffins, vol%	52	71	88	100
Olefins, vol%	0	0	0	0
Naphthenes, vol%	42	20	0	0
Aromatics, vol%	6	9	12	0
	100	100	100	100
N+2A	54	38	24	0

upgrading FT naphtha into high-octane gasoline presents a greater technological challenge (higher costs) than converting heavy FT products into distillate fuels.

MOTOR FUEL OXYGENATES

We mentioned hydrotreating to remove contaminant levels of oxygenates in the preceding discussion. An alternative FT route to motor fuels is converting synthesis gas into oxygenates as the principal product. In this case, oxygenates become the high-octane source instead of aromatics. Lurgi, DOW, and others have developed FT based technologies for producing motor fuel oxygenates [7].

3. FT products as chemicals

When you consider chemical production via FT, the natural starting place is SASOL. SASOL markets over 100 different products, only a handful of which fall into the fuels category. Theo Van Der Pas, General Manager of SASOL, stated "The lack of selectivity of FT towards gasoline and diesel was recognized as an opportunity rather than a disadvantage, and it was decided to spend additional capital to recover the more valuable by-products and so the market value of its products" [8]. A comparison of recent market prices for various fuels and

Table 4
Selected fuel and chemical prices

Item	Comment	Quoted price	$/MT	Source
Crude oil	Average World FOB	17.39 $/bbl	126	a.
Gasoline	NY, 87 octane	21.63 $/bbl	194	a.
Heating oil	No. 2 (Diesel proxy)	24.51 $/bbl	186	a.
LCO	High aromatic	19.3 $/bbl	128	c.
Fuel oil	No. 6	17.75 $/bbl	124	a.
Benzene	Baytown, Tex.	1.25 $/gal	373	b.
Toluene	Baytown, Tex.	0.77 $/gal	223	b.
Xylenes	Baytown, Tex.	0.85 $/gal	259	b.
Ethylene	Contract, delivered	0.25 $/lb	551	b.
Propylene	Gulf Coast	0.16 $/lb	353	b.
1-octene	alpha-olefin	0.40 $/lb	882	c.
1-octanol	Tanks, FOB	0.92 $/lb	2,028	b.
FT wax	Vestowax FT-300 *	1.23 $/lb	2,712	d.

Notes:
a. Oil and Gas Journal (November 27, 1989).
b. Chemical and Marketing Reporter (November 27, 1989).
c. UOP estimate.
d. Price quote from Durachem, Harrison, NY, Jan. 16, 1990.
* Vestowax is a trademark of Chemische Werke Huels.

chemicals reinforces the concept that we should not overlook an opportunity for chemicals production (table 4). The type of chemicals made depends on the following key factors:

Factor	Example
Raw material	Natural gas, coal
FT reactor	Fixed bed, moving bed
Catalyst	Fe, Co
Process cond.	Pressure, H_2/CO

Coal is a more complex raw material than natural glas, and leads to a wider array of by-products. SASOL produces many chemicals from coal gasification, as well as in the actual FT synthesis step. Processes based on natural gas make few by-products in the synthesis gas step. Our focus is on chemicals produced within FT synthesis, so the following discussion applies to any FT feed source.

Choices of reactor design, catalyst, and process conditions determine the nature of the product composition. Carbon number distribution, degree of branching, olefinicity, and oxygenate formation can be adjusted over a wide range. For example, two different commercial synthesis routes used by SASOL make highly branched products from Synthol technology, and virtually all straight-chain products from Arge technology (table 5). The relationship between

Table 5
Comparison of Arge and Synthol products [a]

	Arge	Synthol
Gasoline cut [b]		
Olefins, wt%	32	65
Paraffins, wt%	60	14
Aromatics, wt%	0	7
Alcohols, wt%	7	6
Ketones, wt%	0.6	6
Acids, wt%	0.4	2
Normal paraffins in total paraffin, %	95	55
Diesel cut		
Olefins, wt%	25	73
Paraffins, wt%	65	10
Aromatics, wt%	0	10
Alcohols, wt%	6	4
Ketones, wt%	<1	2
Acids, wt%	0.05	1
Normal paraffins in total paraffin, %	93	60

Notes:
[a] Source: M.E. Dry, Sasol's Fischer-Tropsch experience, Hydrocarbon Processing (August, 1982).
[b] Before hydrotreating.

FT technology and the types of chemicals produced should be evaluated, even if the refiner's primary intent is to produce liquid fuels.

We have chosen two examples of adapting FT technology for the production of valuable petrochemicals. Both examples emphasize the interaction between FT synthesis and subsequent upgrading technologies. In the first example, FT LPG is converted to petrochemical grade BTX aromatics. In the second example, a separations approach is used to recover petrochemicals produced directly by FT.

BTX PETROCHEMICAL PRODUCTION

The standard route to BTX aromatics is naphtha reforming followed by aromatics extraction. As previously described, hydrotreated FT naptha is highly paraffinic, and difficult to reform into aromatics. An alternative route to aromatics is direct conversion of FT LPG with the Cyclar * process [9]. The liquid product from the Cyclar process is essentially free of paraffins and naphthenes, and can be used in most petrochemical conversions after simple fractionation.

UOP conducted a pilot plant study with olefinic LPG blends, consistent with published Arge and Synthol LPG compositions [5]. Olefins are more easily converted to aromatics than paraffins in the Cyclar process, resulting in higher liquid product yields. This situation permits more flexibility in choosing process conditions, particularly with respect to process pressure. Fig. 8 shows the product yields and liquid product distribution obtained with an olefinic LPG blend. Notice the high percentage of BTX aromatics relative to Ag + liquid product.

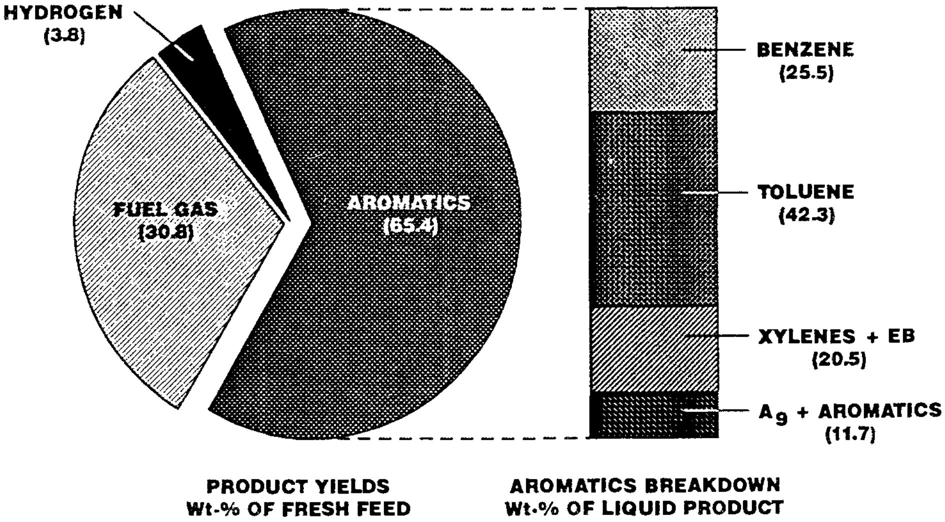


Fig. 8. Aromatics production from FT LPG.

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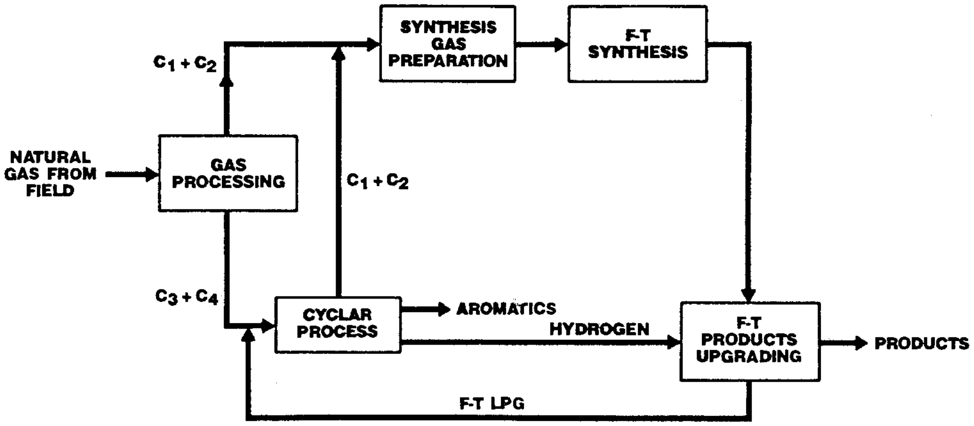

Fig. 9. Integration of Cyclar process into natural gas based FT.

In a FT complex based on natural gas feed, Cyclar has interesting integration potential with the gas reformer (fig. 9). Cyclar could process LPG from the gas field, the FT unit, and the FT upgrading complex. Olefins from the FT reactor are utilized to improve the overall performance of the Cyclar unit. A valuable co-product, hydrogen, is produced in addition to the liquid product. Fuel gas, a by-product from the Cyclar unit, is sent to the gas reformer. On a carbon-mass basis, the Cyclar by-product has the same value as the feedstock assuming that the LPG would otherwise be feed to the gas reforming.

LINEAR OLEFIN AND ALCOHOL PRODUCTION

We have chosen a ruthenium FT catalyst with high selectivity to valuable petrochemical products for this example [10]. Process conditions and the product

Table 6
Ruthenium FT catalyst performance

FT process conditions	
H_2/CO, molar	2.0
GHSV, 1/hr	150
Pressure, ATM	62
Inlet temperature, ° C	208
CO conversion, %	80
$C_4 - C_{18}$ product characteristics	
Paraffins, wt%	43
alpha-olefins, wt%	24
Internal olefins, wt%	5
Primary alcohols, wt%	24
Aldehydes, wt%	4
Linear molecules, %	> 98
Branched molecules, %	< 2

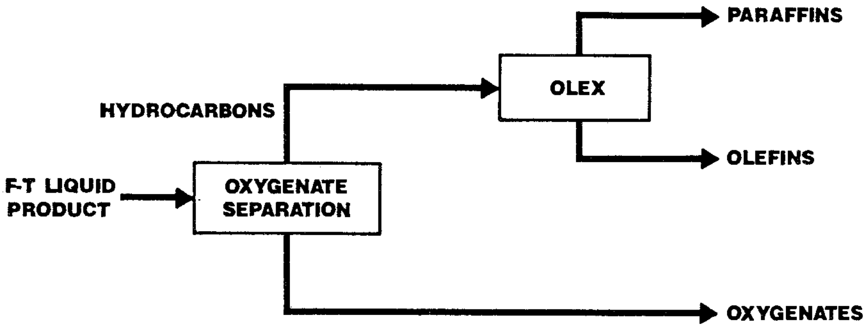

Fig. 10. FT product separation.

distribution are summarized in table 6. Over 98% of the products are linear. Linear paraffins, a-olefins, and alcohols are all valuable products. In a commercial situation, there would be a strong economic incentive to separate the FT product mixture into separate components.

Unfortunately, there is no commercial process for separating a FT product stream into distinct hydrocarbon and oxygenated components. If such a process were developed, recovery of linear primary alcohols and olefins would be possible (fig. 10). The key is to remove the oxygenates intact, without saturating the olefins such as in a hydrotreating step. The hydrocarbon stream is then sent to a UOP Olex * unit. Olex is a commercially proven technology that separates paraffin and olefin mixtures [11]. With the FT product described above, the Olex extract would contain linear olefins. As opposed to ethylene oligomerization, primary linear olefins produced by FT are not limited to even carbon numbers. The Olex raffinate would consist of normal paraffins.

4. Integration of FT into the expanded view of refining

FT fits into the expanded view of refining from a variety of vantage points. Beginning with raw material input, FT reduces the refiner's dependency on a single material, crude oil. Assuming that all carbon sources do not move *identically* in price, multiple feed sources reduce a refiner's raw material cost risk. Risk-adjusted cost of capital is an important component of net present value. If a refiner reduces risk and maintains return, the owners (shareholders) benefit directly. Aside from this financial aspect of providing for multiple feedstocks, governments and consumers would benefit from the refiner's access to multiple forms of energy.

On the output side of the refinery, we have discussed how the desirable features of FT distillate fit into the alternative view. We also mentioned that lighter FT products may have excellent potential as a route to petrochemicals. It is certainly not necessary to choose between fuels and petrochemical production

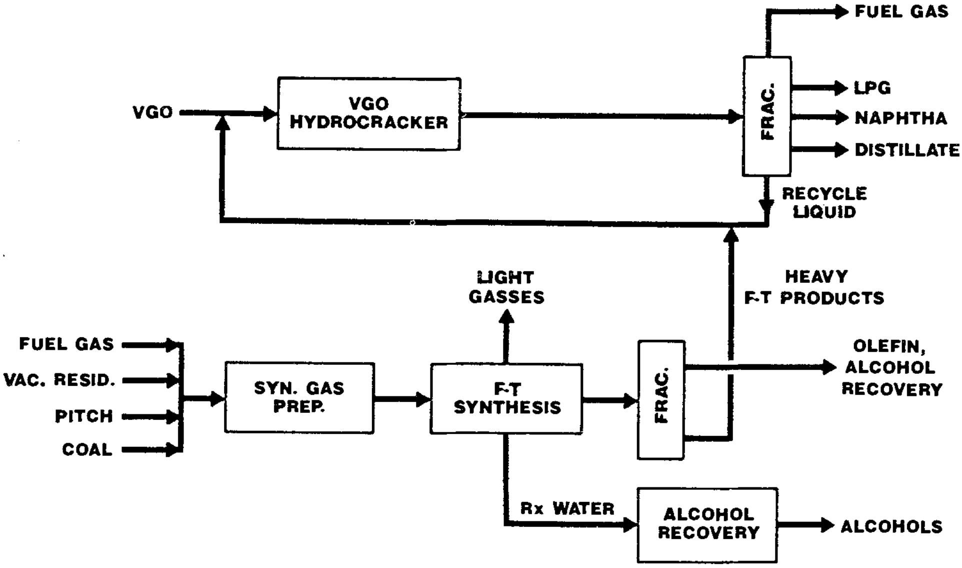

Fig. 11. Integration of FT with existing VGO hydrocracker.

for the entire complex. Instead, it is only logical to utilize the particular strengths of any portion of the FT product spectrum.

We close with an example of integrating FT into an existing refinery (fig. 11). Some potential advantages of this integration include:

1. The addition of FT wax into a VGO feed stream helps the refiner meet aromatics ceilings on diesel fuel. Simultaneously, the overall cetane index of the diesel product improves.
2. Jet fuel produced by the integrated operation has an improved smoke point as a result of lower aromatics.
3. The hydrocracker's fractionator offers a means of separating the broad boiling range product, inherent to FT operation. The advantage is that the FT unit would not require separate fractionation equipment. Of course, the existing fractionatory may require modification.
4. Synthesis gas feed to the FT unit could be derived from coke, pitch, vacuum residuum or some other low-value carbon source. The FT unit could also use any excess fuel gas produced by the refinery. Also, combining feeds with low and high hydrogen contents (pitch and fuel gas) provides a means of adjusting H_2/CO other than water gas shift.
5. The refiner has the option of recovering valuable petrochemicals from the FT product stream.

The best way to evaluate the potential advantages of FT is by taking a broad perspective of the refining industry, with an eye towards future raw material supply situations, and future product market needs.

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