CHAPTER VI

Fischer-Tropsch Refineries

The historical development of commercial Fischer-Tropsch refineries is documented. The German technology (1930-1940's), Hydrocol (1940-1950's), Sasol 1 (1950's), Sasol 2 and 3 (1970-1980's), Mossgas (1980-1990's), Shell Bintulu (1980-1990's) and Oryx GTL (2000's) are all discussed in terms of their Fischer-Tropsch synthesis, gas loop and refinery designs. The evolution of the commercial refineries that are still in operation is also described to show how external factors influenced modifications to the refinery design. It is shown that the same change drivers that affect crude oil refineries also affect Fischer-Tropsch refineries, but that different variables are introduced by options like feedstock choice (GTL or CTL), gasification technology (tar products or not), Fischer-Tropsch synthesis (HTFT or LTFT), product slate (fuels, chemicals or both) and market (final or intermediate products).

1. Introduction

The development of Fischer-Tropsch refineries should be seen in historical context. The German LTFT refineries, the USA Hydrocol HTFT refinery and the South African Sasol 1 HTFT-LTFT combination refinery were built before the 1970's, in the time when most crude oil refineries were still 2nd generation topping-reforming type refineries. It should further be noted that Fischer-Tropsch catalyst development is much like oil exploration and generally takes place in isolation, not being sensitive to its impact on refining. Fischer-Tropsch refinery designs are therefore truly a reflection of the transformations that were needed to convert syncrude into products that met the market demands of their time.

Few Fischer-Tropsch technologies were developed to the point where either a demonstration scale pilot plant, or a commercial Fischer-Tropsch refinery was built. The Fischer-Tropsch refineries that will be described are all commercial facilities. During the discussion, reference will be made to the Fischer-Tropsch technology and the syncrude composition, since it is pertinent to the refinery design. The basis for the Fischer-Tropsch technology selection, as well as the design philosophy for the refinery will be highlighted.

Apart from the Sasol refineries in South Africa, all other Fischer-Tropsch refineries that were built before the 1990's are no longer in operation. Unlike the post-1990 refinery designs and those of the period 1930-1950 that are mainly of historical interest, discussion of the refinery designs of the 1950-present period presents a moving target. The older Fischer-Tropsch refineries that are still operational, had to evolve to keep pace with changes in the market and the legislation governing transportation fuels. The evolution of these refineries will be dealt with separately from the description of the original design.

It is highly likely that existing Fischer-Tropsch refineries will continue to change and that future refineries will be different to those constructed since the 1990's. Predictions about the future of Fischer-Tropsch refining is more difficult to make than for crude oil refining, because it presents such a small sample. This topic will nevertheless be briefly discussed to serve as an introduction to the chapters on technology selection and refinery design.

2. German technology (1930-1940's)

German Fischer-Tropsch research focussed mainly on iron, cobalt and thorium,[a] while studies using ruthenium and nickel were limited to initial laboratory work.(1)(2) Although the initial work was done with iron, cobalt proved easier to develop and all commercial German Fischer-Tropsch plants were based on cobalt catalysts.[b,(1)(3)] Interest in iron based Fischer-Tropsch was revived only during the Second World War, when cobalt became increasingly scarce.

Two processes were developed based on the Fischer-Tropsch catalyst: a normal-pressure (<0.1 MPa) process and a medium-pressure process (1-2 MPa). The German Fischer-Tropsch plants were all built in the period 1935-1938 and initially made use of the normal-pressure process. Development of the medium-pressure process started in 1937 and was tested on large scale in 1939 by Lurgi in the Hoesch plant.(5) Conversion of a further two commercial scale plants were reportedly planned. Ruhrchemie further developed the medium-pressure process, but in 1944, before conversion of the Holten Sterkrade plant to medium pressure operation could be completed, it was destroyed by bombing.(2) In a more recent summary of the German FT production capacity these conversions were indicated,

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[a] The thorium based Fischer-Tropsch catalysts were selective for short chain branched products and it was called the "Iso-synthesis" process. This made it ideal for high octane gasoline and research on this process was reportedly begun in 1941 at the Kaiser Wilhelm Institut für Kohlenforschung. Other oxides and combinations thereof could also be used, but required the complete absence of iron-group metals, even in trace quantities.

showing seven normal-pressure and four medium pressure plants spread among the nine German Fischer-Tropsch production sites.(6) (Literature seems to be contradictory).

Work on Fischer-Tropsch technology continued in Germany after the Second World War and amongst other things led to the development of the first slurry bed technology in 1953.(7) A detailed history and description of the German Fischer-Tropsch developments has recently been published by Davis.(8)

2.1. Normal-pressure cobalt Fischer-Tropsch synthesis

The flow diagram of a German normal-pressure Fischer-Tropsch synthesis plant is given in Figure 1.(4) Not all plants used the same synthesis gas production methodology, but due to the sulphur sensitivity of the Fischer-Tropsch catalyst, all were required to purify the gas before use. A H_2:CO ratio of 2:1 was required for synthesis and a water gas shift-reactor was used to adjust the H_2:CO ratio of the purified gas.

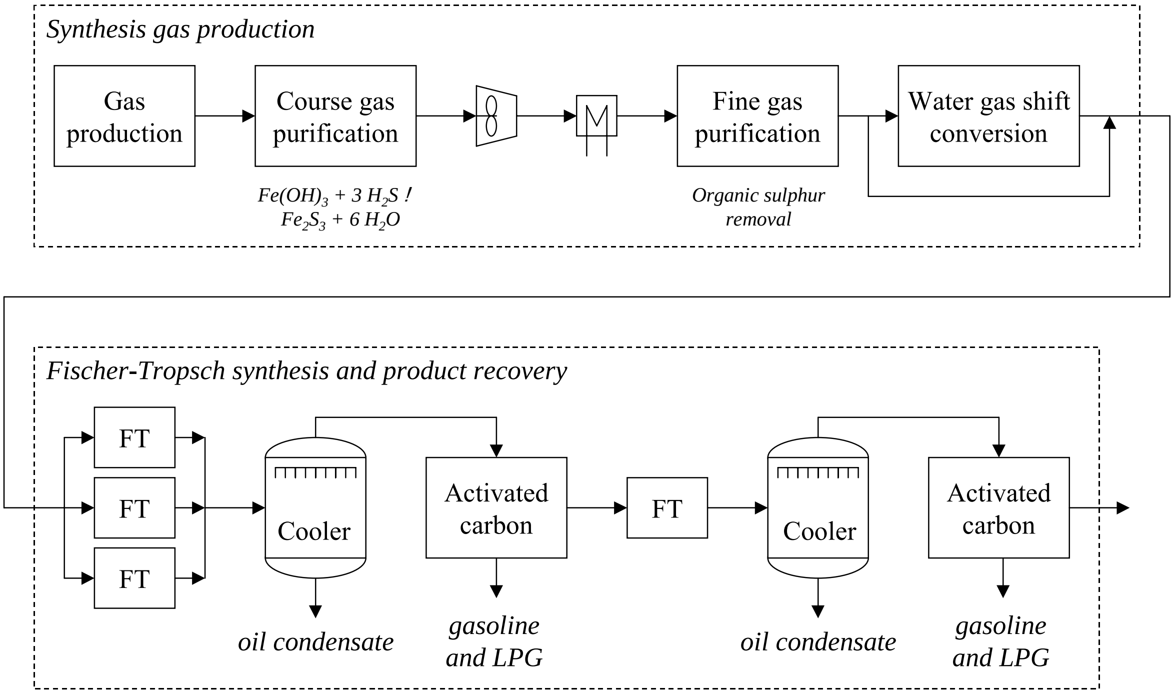

Figure 1. Flow diagram of a German normal-pressure Fischer-Tropsch synthesis plant.

The normal-pressure Fischer-Tropsch reactors were about 5 m long, 2.5 m wide and 1.5 m high. Each reactor consisted of tubes and heat transfer plates, with the catalyst being loaded on the shell-side between the heat transfer plates (Figure 2).(2)(4) Water was circulated

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[b] The precipitated cobalt Fischer-Tropsch catalyst used in German technology consisted of a mixture of cobalt-thoria-magnesia-kieselguhr in 100:5:10:200 ratio.

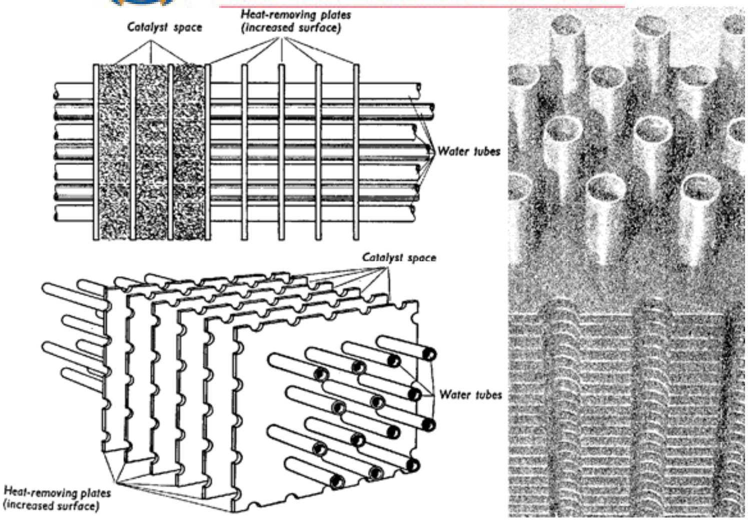

Figure 2. Internals of a normal-pressure Fischer-Tropsch reactor. (These figures have been reproduced directly from Refs.(2) and (4), and are copyright protected).

in the tubes to regulate the temperature. The catalyst bed was typically operated 5-8°C higher than the temperature in the tubes and in practise the reactor temperature could be controlled to within 1°C in the range 170-200°C by regulating the water pressure, using a boiler principle.[c] The synthesis gas pressure in the reactor was around 30 kPa.(4) The German normal-pressure Fischer-Tropsch technology can therefore be classified as a low temperature Fischer-Tropsch (LTFT) process.

In order to achieve a reasonable synthesis gas conversion,[d] normal-pressure plants used two or three Fischer-Tropsch synthesis stages in series. The German cobalt Fischer-Tropsch catalyst typically had a lifetime of 4-6 months, but temporary deactivation due to blockage by wax required "regeneration" every 700 hours. This entailed catalyst washing by spraying it with kerosene (180-230°C boiling range) to extract the wax. The product thus obtained was called catalyst wax.

A product recovery section followed each synthesis stage. The product was cooled down by spray-condensers to ambient conditions to yield an oil fraction, before the uncondensed gas was passed over a bed of activated carbon. The gaseous hydrocarbons were adsorbed on activated carbon from which it was recovered batch-wise by steaming (Figure 3).(4) The desorbed product was then stabilised by pressure distillation to yield an active carbon gasoline and liquid petroleum gas (LPG). The composition of the syncrude fractions from such a normal-pressure process is given in Table 1.[e,(4)] In addition to the hydrocarbon

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[c] In the German design the tubes could withstand a pressure of 3 MPa. The heat release during Fischer-Tropsch synthesis is about 150 kJ·m^{-3} synthesis gas, which is equivalent to about 1.5 MJ·kg^{-1} of product.

[d] Conversion on average yielded in the order of 0.1 kg product per 1 m^3 of gas.

[e] The kerosene (180-230°C) was called Kogasin I, while the diesel (230-320°C) was called Kogasin II.

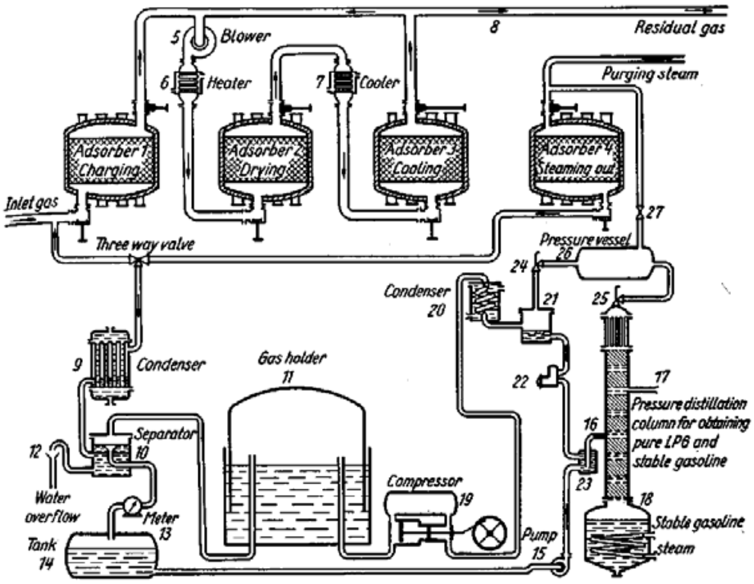

Figure 3. Activated carbon product recovery section after each Fischer-Tropsch synthesis stage. (This figure has been reproduced directly from Ref.(4) and is copyright protected).

products, the syncrude also contained oxygenates, mostly alcohols and carboxylic acids, which gave it a characteristic smell.

Table 1. Syncrude composition from German normal-pressure Co Fischer-Tropsch synthesis.

Description	Catalyst wax	Condensate oil	Carbon gasoline [‡]	Crude LPG	Olefin content
Mass of total product (%)	2	40	50	8	
CO_2				10-30	
CO				1-3	
H_2				2-4	
methane				2-3	
ethane and ethylene				1-2	
propane and propylene			1	15-20	43
C_4 hydrocarbons			5-15	20-40	
C_5 hydrocarbons			15-20	10-20	37
C_6-180°C fraction		1-3	20-25	3-5	
180-230°C fraction (Kogasin I)		35-40			18
230-320°C fraction (Kogasin II)		30-35			8
320-460°C fraction (Slack wax)	20-30	20			0
>460°C fraction (Hard wax)	70-80	1			0

[‡] In the source reference the carbon gasoline does not add up to 100%, since the remainder is mainly gaseous products.

2.2. Refining of normal-pressure syncrude

The German normal-pressure Fischer-Tropsch process was originally considered a motor-gasoline synthesis process and product work-up was directed exclusively to this end. The reason behind this thinking is clear from the product distribution of the commercial processes (Table 2).(4) The light olefins (C_3-C_4) were converted to chemicals, like alcohols, while the low octane motor-gasoline and high cetane distillate fractions were used as fuel blending components.(2) It was later recognised that the middle distillate paraffins can also be used for substitution reactions and that the slack wax has value as starting material for lubricating oil production, as well as products from autoxidation.(2)(4)

Table 2. Product distribution from the Rheinpreussen plant in Germany.

Product	Mass %
Liquid petroleum gas, LPG (C_3 and C_4)	10
Motor-gasoline (C_5-180°C)	52.2
Diesel fuel (180-320°C)	26.5
Soft paraffin wax (320-460°C)	7.6
Hard paraffin was (>460°C)	3.7

The Fischer-Tropsch refineries used in conjunction with the German normal-pressure Fischer-Tropsch process differed mostly in the processing of the heavier fractions and the sequence of the processing steps. A basic flow-diagram showing the main conversion steps is given in Figure 4. This does not represent any specific German Fischer-Tropsch refinery, but rather a general refinery configuration.

Table 3. Liquid phosphoric acid oligomerisation of Fischer-Tropsch derived propylene at 180-200°C and 4-6 MPa, as practised by I.G. Farbenindustrie during the Second World War in Germany to produce hydroformylation feed.

Description	Boiling range (°C)	Yield (mass %)
Dimers	60-130	15-20
Trimers	130-180	35-40
Tetramers	180-200	29
Higher olefins	200-260	16

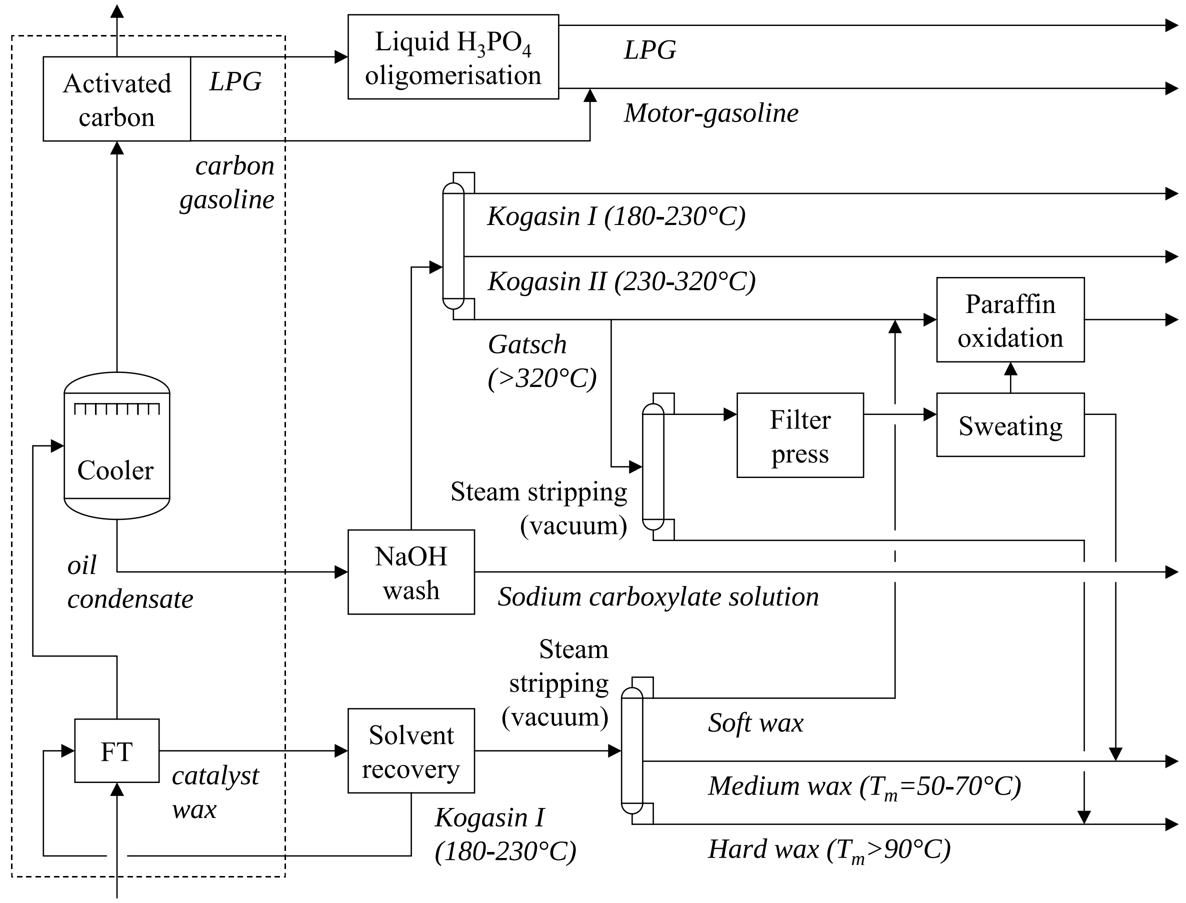

Figure 4. Generic German normal-pressure Fischer-Tropsch refinery.

The light olefins were converted by either a phosphoric acid oligomerisation, or aluminium chloride based oligomerisation processes. Liquid phosphoric acid oligomerisation was chiefly employed to produce dimers, trimers and tetramers of propylene and butenes that could be hydroformylated[f] and hydrogenated to detergent range alcohols. The method practised in Germany used a reactor consisting of three silvered tubes connected in series in a single water-cooled reactor,[g] yielding an oligomeric product in the desired range (Table 3).(9) Aluminium chloride oligomerisation was used to produce synthetic lubricants. The feed to this process was not only obtained from the LPG fraction, but also from cracking. Ruhrchemie used the Kogasin II fraction and thermally cracked it in the presence of steam at 550-600°C, before oligomerising it over $AlCl_3$ (Figure 5).(9)(10) A variation of this was practised by Établissements Kuhlmann in France starting with Fischer-Tropsch gasoline.(9)

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[f] Alcohol manufacture was typically done by the OXO process, discovered by Otto Roelen of Ruhrchemie in 1938, which is the hydroformylation of olefins with CO and H_2 to produce aldehydes.

[g] Each tube was 5 m high and had a diameter of 0.18 m. Each tube was loaded with 40 kg of acid and 70 kg of oligomer to about one third of its height. The olefinic feed was pumped through the tubes with an inlet pressure of 6 MPa and outlet pressure of 4 MPa. Reaction took place at 180-200°C and olefin conversion of 90% was typically achieved. Entrained phosphoric acid was separated from the product and recycled.

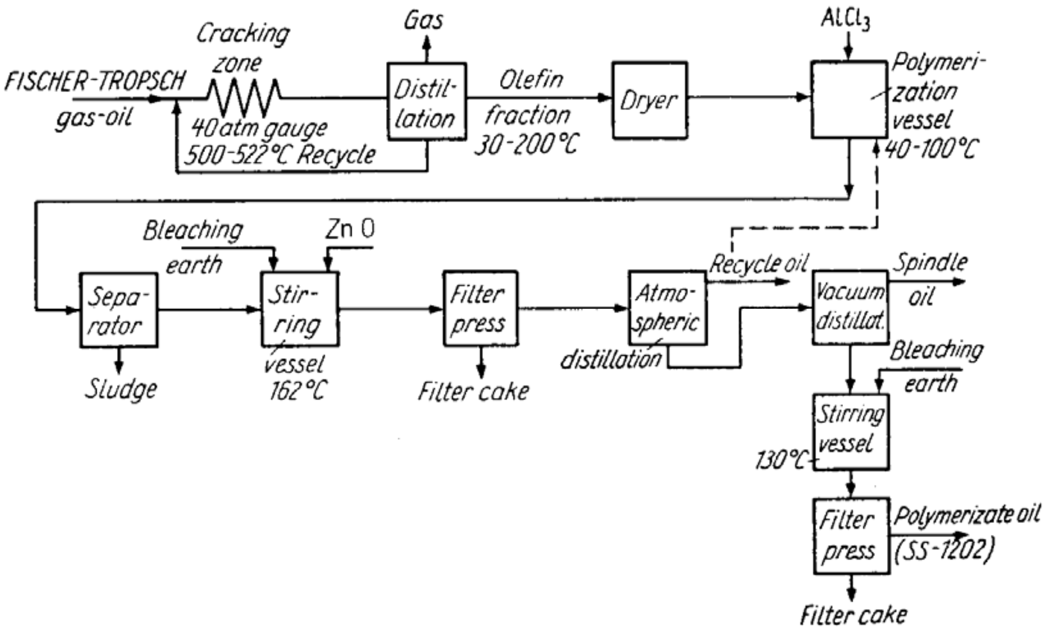

Figure 5. Cracking of Kogasin II and $AlCl_3$ oligomerisation to produce lubricating oil. (This figure has been reproduced directly from Ref.(4) and is copyright protected).

The straight run motor-gasoline from the Fischer-Tropsch process had a low octane number, with the 30-110°C cut having a MON of 67 and the 30-140°C a MON of 62.$^{(2)}$ Initially, in 1938, the octane value was improved by mixing it with aromatics and alcohol, but later Ruhrchemie added two True-Vapour-Phase processes[h] with gas recycle to convert the higher boiling fractions to gasoline with a much higher octane number, for example the 30-165°C fraction had a MON of 75.$^{(11)}$ The construction of a catalytic cracking plant to produce C_3-C_5 olefins from C_7+ Fischer-Tropsch fractions to be oligomerised to motor-gasoline (by phosphoric acid catalysis) was abandoned in mid-1944.$^{(2)}$ An evaluation of the products from such a process was done before the Second World War.$^{(12)}$

Condensate oil contained some carboxylic acid that was removed by a caustic wash. The aqueous wash solutions contained sodium carboxylates in addition to hydrocarbons, iron[i] and other impurities.$^{(1)}$ The carboxylates were recovered and used for greases, soaps, etc. The acid-free organic product was distilled to produce various fractions. The Kogasin I fraction was combined with the heavy gasoline and used as diesel fuel.[j] It was a quite light diesel (155-250°C), with good cetane number (75-78) and low density (743-749 kg·m^{-3}), but according to Weil and Lane$^{(2)}$ it did not make a very good diesel fuel, although no specific

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[h] Thermal cracking and oligomerisation of the short chain olefins. Operating conditions of 540°C and 0.3-0.5 MPa, with a residence time of 100-200 s.

[i] Since a cobalt based Fischer-Tropsch catalyst was used, it is likely that the iron was due to acid corrosion.

[j] The motivation behind the use of heavy gasoline in the diesel is not known with certainty, but probably due to a lack of motor-gasoline octane improving technologies in the Fischer-Tropsch refinery and the need to use the molecules in the detergent range (C_{12}-C_{15}) for detergents. Ref.(2)

reasons were given.[k] A detailed analysis of the diesel fuel from the Carrières Kuhlmann FT plant at Harnes in France showed a heavier product (195-310°C) consisting of Kogasin I and Kogasin II, with a density at 20°C of 768 $kg \cdot m^{-3}$ and cetane number of 80.(13) The diesel contained 2% oxygenates, mostly alcohols, carbonyls and carboxylic acids, but it also contained some esters and phenolic compounds.

The Kogasin II fraction was used as feedstock for thermal cracking to make lubricating oils(14) when not used as diesel fuel. The bottom fraction from distillation (gatsch or slack wax) was either being used as feedstock for paraffin oxidation and fatty acid manufacture, or steam stripped to produce medium and hard wax products. The hard wax had a small market as ceresin wax, but in general had little use, while the medium wax could be used for candles, etc. The catalyst wax was also steam stripped to produce a soft, medium and hard wax fraction. The characteristics of these wax products have been reported.(15)(16)

3. United States technology (1940-1950's)

Subsequent to the Second World War, much technical information about the German Fischer-Tropsch technology became available in the United States. During this period Hydrocarbon Research Inc. developed an American version of the Fischer-Tropsch process, called the Hydrocol process.(17) This process used an iron based Fischer-Tropsch catalyst in a fixed fluidized bed reactor.(4) The process was piloted at Olean, New York, and led to the construction of the first commercial scale Fischer-Tropsch plant in the USA at Brownsville, Texas by the Carthage Hydrocol Co. This plant was in operation during the period 1951-1957 and was shut down mainly due to economical reasons.(20) A second plant was planned by Standolind Oil and Gas Co. for Hugoton, Kansas, but was never built.(21)(22) Around the same time Philips Petroleum Co. also started development of an iron based fluidised bed Fischer-Tropsch process, which was piloted at their research facilities in Bartlesville, Oklahoma, but this process was never commercialised.(23)(24) Various other companies also had research programmes and some are still active in the field of Fischer-Tropsch research.(8)

Apart from the commercial interest in Fischer-Tropsch technology in the United States, the strategic value of this technology was recognised at government level. Prior to the Second World War, Fischer-Tropsch research was funded by the United States government.

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[k] It is speculated that the evaluation was performed on a comparative basis without compensating for the low density and viscosity of the Fischer-Tropsch product. This would result in lower power output, as was indeed reported elsewhere. Ref.(6)

This process was accelerated when the U.S. Bureau of Mines was tasked by the United States Congress[l] to find an alternative to crude oil as source for transportation fuel.(22) Fischer-Tropsch and coal liquefaction were investigated in parallel, since it was unclear which of these technologies were the most economical. Although demonstration scale operation was terminated in 1953, after substantial new oil reserves were discovered in the United States, Canada and Middle East, pilot plant studies were continued at the Pittsburgh Energy Technology Centre.(25) Work on Fischer-Tropsch has been continuously sponsored by the United States Department of Energy.

3.1. Hydrocol Fischer-Tropsch synthesis

The Hydrocol plant made use of natural gas as feedstock for the production of synthesis gas by partial oxidation of the methane with oxygen.[m] The basic flow diagram of the Hydrocol process is given in Figure 6.(17) The first step is separation of the condensable liquids from the natural gas. This is followed by synthesis gas production. The synthesis gas was not purified after production, but was directly used for Fischer-Tropsch synthesis, despite the presence of sulphur compounds in the synthesis gas. The omission of a gas purification step was nevertheless possible, because the design of the Fischer-Tropsch reactor allowed the replacement of deactivated Fischer-Tropsch catalyst on-stream,[n] not because of the low sulphur content of the natural gas.

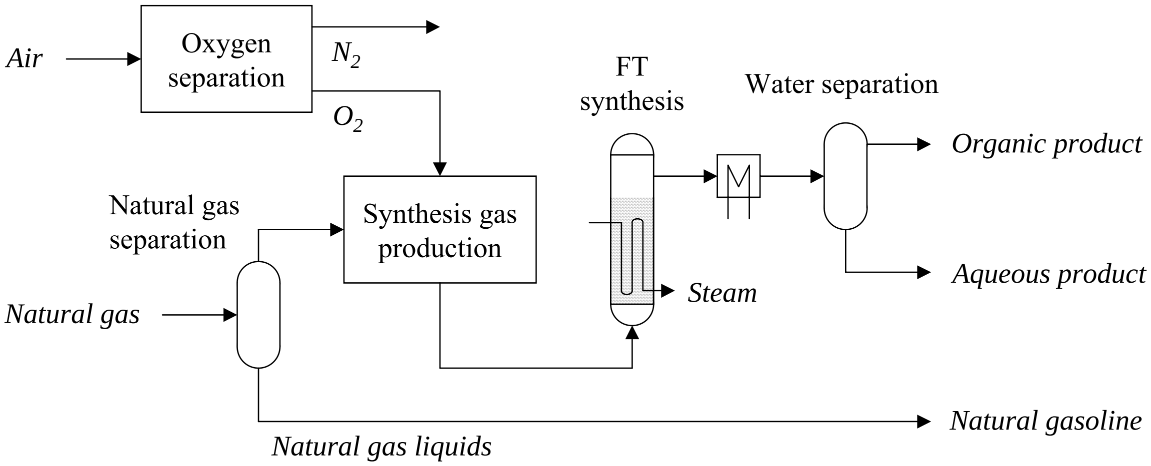

Figure 6. Flow diagram of the Hydrocol synthesis section.

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[l] On 5 April 1944 the “Synthetic Liquids Fuels Act” was passed by the United States Congress.
[m] The oxygen plant that was erected, was the largest in the world at that time.
[n] This ability proved to be more theoretical than practical.

The Fischer-Tropsch catalyst used in the Hydrocol process was a fused iron catalyst that was also used for ammonia synthesis, consisting of 97% Fe_3O_4 (magnetite), 2.5% Al_2O_3 and 0.5% K_2O. It was later replaced with a natural magnetite containing 0.5% K_2O. The catalyst was ground to a fine powder (0.045-0.45 mm) and was completely reduced at 350-460°C in hydrogen before use.(4) The synthesis gas was produced from non-catalytic combustion of natural gas with oxygen to produce a synthesis gas with H_2:CO ratio of approximately 2:1.(18) The Hydrocol plant used two 5 m diameter synthesis reactors.(19) The synthesis reactors were of a two phase fixed fluidised bed design with a heat exchanger suspended in the bed to control the temperature by producing 2.1-2.8 MPa steam. The surface of the fluidised catalyst bed remained fairly smooth during operation, although local eruption of bubbles could be seen. Little catalyst was carried away with the product gas.. The reactor was operated in the range 305-345°C and 2.8-4.5 MPa,[o] with a linear gas velocity of 0.2 $m \cdot s^{-1}$.(4)(20). This technology is therefore classified as a high temperature Fischer-Tropsch (HTFT) process.

The product from Hydrocol synthesis consisted mainly of motor-gasoline range products (Table 4).(18) The production of heavy products had to be avoided, since they would cause product condensation, catalyst agglomeration and then bed slumping in the synthesis reactor. This is a general restriction imposed on the α-value of Fischer-Tropsch catalysts used in technologies making use of fluidised bed reactors.

Table 4. Composition of the synthesis product from the Hydrocol process.

Description	Mass %	Olefinicity (%)
Liquid petroleum gas, LPG (C_3 and C_4)	32	82
Naphtha (C_5-204°C)	56	85-90
Distillate	8	75-85
Residue	4	-

The hydrocarbons produced by the Hydrocol process were rich in linear α-olefins and in general the products had a low degree of branching (Table 5),(4)(18) with the methyl branched products being mainly 2-methyl isomers.(26) In addition to the hydrocarbon products, oxygenates were also produced. The water-soluble oxygenates were mainly ethanol and acetic acid, with lesser amounts of acetone, acetaldehyde and higher alcohols

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[o] Conversion of about 90% was achieved, with about 0.15 kg C_3+ hydrocarbons per 1 m^3 of synthesis gas being produced. The overall reactor productivity was around 180 $kg \cdot h^{-1}$ per m^3 of catalyst.

being produced. With increasing carbon number, more oxygenates are found in the organic phase (Table 6).(4)(27) Since it is an HTFT process, aromatics were also produced.

Table 5. Degree of branching in the products from the Hydrocol process.

Carbon number	Linear	Methyl branched	Dimethyl branched	Cyclic
C_4	89.4	10.6	-	0.0
C_5	80.9	18.8	0.0	0.3
C_6	75.9	20.0	0.4	3.7
C_7	60.2	29.3	1.7	8.8
C_8	55.4	36.6	2.4	5.6

Table 6. Distribution of compound classes in the oil fraction of Hydrocol syncrude (mass %).

Carbon number	Distillation range (°C)	Paraffins (%)	Olefins (%)	Aromatics (%)	Oxygenates (%) ‡
C_3		20.2	79.8	-	-
C_4		15.5	84.5	-	-
C_5	15-40	15.4	81.8	0	2.8
C_6	40-75	13.2	80	0.2	6.6
C_7	75-104	10.5	80.2	2.1	7.2
C_8	104-138	9.6	76.2	6	8.2
C_9	138-162	1.8	79	6.2	13
C_{10}	162-187	6	79.3	7.2	7.5
C_{11}	187-200	9.3	74	5.8	10.9
C_{12}	200-220	5.4	76.5	3.6	14.5

‡ Oxygenates were calculated by difference.

3.2. Refining of Hydrocol syncrude

The aim of the Hydrocol process was to produce high-octane motor-gasoline with a better than 80% yield of the syncrude. This is an important statement of intent, since it requires the refining steps to produce a product that could meet the octane requirements of the 1950's after the addition of tetraethyl lead (TEL). Apart from normal oil product separation, the refinery had to include conversion and separation steps that addressed issues specific to the Hydrocol process,(2) namely:

a) Removal of the unwanted oxygenates from the organic product and especially the carboxylic acids that were known to cause problems.(28)

b) Increase the octane number of the straight run syncrude (RON=62, MON=68)(18) to a higher value that could be upgraded to meet an 80 MON specification by TEL addition.[p]

c) Convert the gaseous olefins (C_3-C_4) to liquid products, since it constituted about one third of the product from Hydrocol synthesis.

d) Recover the alcohols and other valuable oxygenates dissolved in the aqueous product to be sold as chemicals.(26)

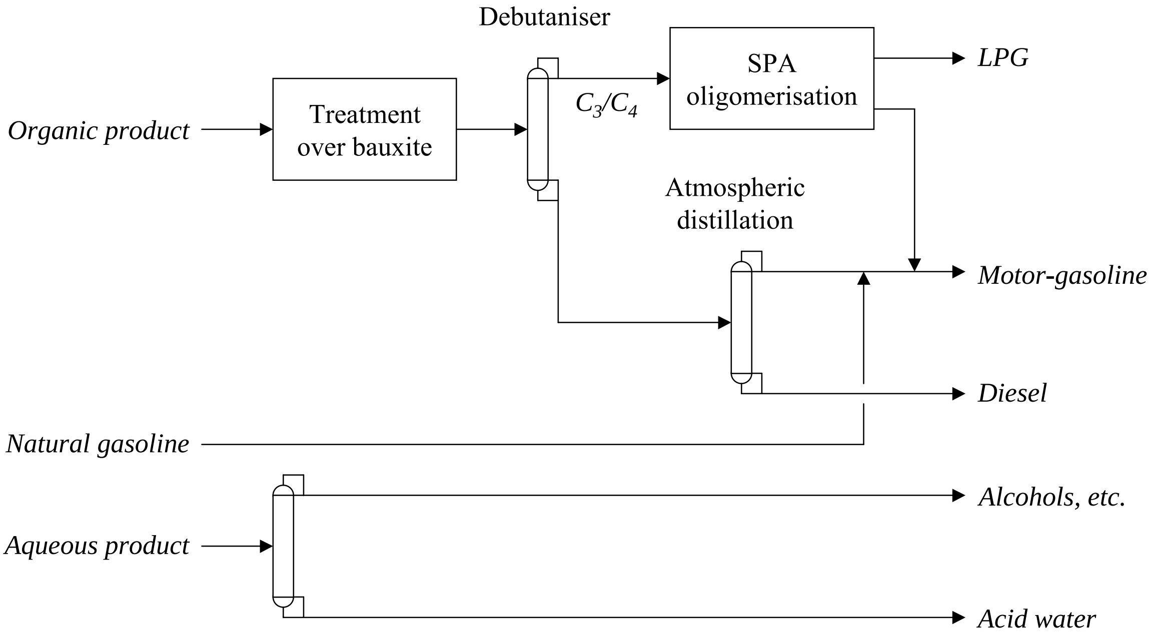

Figure 7. Flow diagram of the HTFT Hydrocol refinery.

The flow diagram of the Hydrocol refinery is shown in Figure 7. The first organic phase processing step involved oxygenate removal over bauxite at a temperature around 400°C.(18)(28) Bauxite is a natural silica-alumina consisting of 30-75% Al_2O_3, 2-9% SiO_2, 3-25% Fe_2O_3, 1-3% TiO_2 and 9-31% H_2O.(29) This bauxite treatment step was a commercial process, called the Perco-process, which was used as a sulphur removal step in oil refineries.(30) It was also used for oxygenate removal from the syncrude produced in the Philips Petroleum HTFT pilot plant.(24) Very good results were obtained with this process, since it not only removed the oxygenates, but also increased the octane number of the naphtha (RON=87 and MON=76).[q] The improvement in octane number is mainly due to

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[p] With the addition of 3 ml TEL per gallon of straight run Hydrocol syncrude, the RON=84 and MON=74.

[q] With the addition of 1 ml TEL per gallon of bauxite treated Hydrocol syncrude, the RON=93 and MON=80.

double bond isomerisation of the α-olefins to internal olefins and a more detailed description of the reactions involved in this process is given elsewhere.(31)

The C_3-C_4 olefins were converted to polymer gasoline over a solid phosphoric acid catalyst in the UOP CatPoly process(32) at 205°C, 3.5 MPa and LHSV of 1.15 h^{-1}.(18) The unhydrogenated motor-gasoline from such a process is fairly insensitive to the feed material and operating conditions used(33) and had a RON=95 and MON=82.(18)

The Hydrocol refinery also included cross-platform integration, since the natural gas derived naphtha (natural gasoline) was blended with the Fischer-Tropsch derived synthetic motor-gasoline. The distillate fraction was not upgraded any further and reportedly had a cetane number of 45-50 and pour point of less than –15°C.(2) It was nevertheless shown that this product could be upgraded by hydrogenation to have a cetane number of 71 and a pour point of –1°C.(34)

The upgrading of the aqueous product was investigated, but it was soon realised that many of the carbonyls and alcohols formed azeotropes on distillation.(26) The chemical potential of HTFT was therefore realised in principle, but required extensive investigations to be realised in practise, mainly due to the absence of binary and ternary phase diagrams.

4. Sasol 1 technology (1950's)

The Fischer-Tropsch work of P. C. Keith[r] of Hydrocarbon Research Inc., which formed the basis for the Hydrocol process, also interested Anglovaal. In 1945 Anglovaal officially informed the South African government of its intentions to build a coal-to-liquids plant in South Africa. Although a licence to produce synthetic fuels was officially given to Anglovaal in 1949, it became apparent that a venture of this magnitude would be difficult to finance without government support. It was also realised that such a venture was in national interest. This led to the formation of a new company called Sasol in 1950.[s]

During this period the technology selection for the synthetic fuels process was already under way. Five proposals were considered, of which only the proposals of the Arbeitsgemeinschaft Ruhrchemie-Lurgi (Arge) in Germany and Kellogg in the United States were found to be technically sound enough. It was realised that the HTFT Kellogg proposal would be much cheaper to implement, but that the LTFT Arge proposal brought all the

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[r] P. C. Kieth originally worked for M. W. Kellogg before forming the Hydrocarbon Research Inc. company and the Hydrocol process was a variant of the HTFT Kellogg technology.

German commercial experience to the table and the latter was therefore a much safer option. Eventually both proposals were accepted and Sasol 1 was constructed using two thirds American and one third German technology. Initially it was thought to run the processes in parallel, but separately, but in order to exploit the synergism between the HTFT Kellogg and LTFT Arge technologies, the two processes were integrated.(35)

Construction of the Sasol 1 facility started in the middle of 1952 at the place now called Sasolburg, which is about 100 km south of Johannesburg. Commissioning of the air separation plant, power generation plant and Lurgi gasifiers started in 1954, but the synthesis section and refinery were only commissioned in 1955.[t] Although the subsequent discussion will deal primarily with the original Sasol 1 design, it is noteworthy that some of the original units in the Sasol 1 facility are still operational more than 50 years later.

4.1. Kellogg Fischer-Tropsch synthesis

The Kellogg Synthol[u],(36) HTFT design made use of a fused iron catalyst that was operated in a circulating fluidised bed (CFB) reactor (Figure 8). These reactors had been developed by

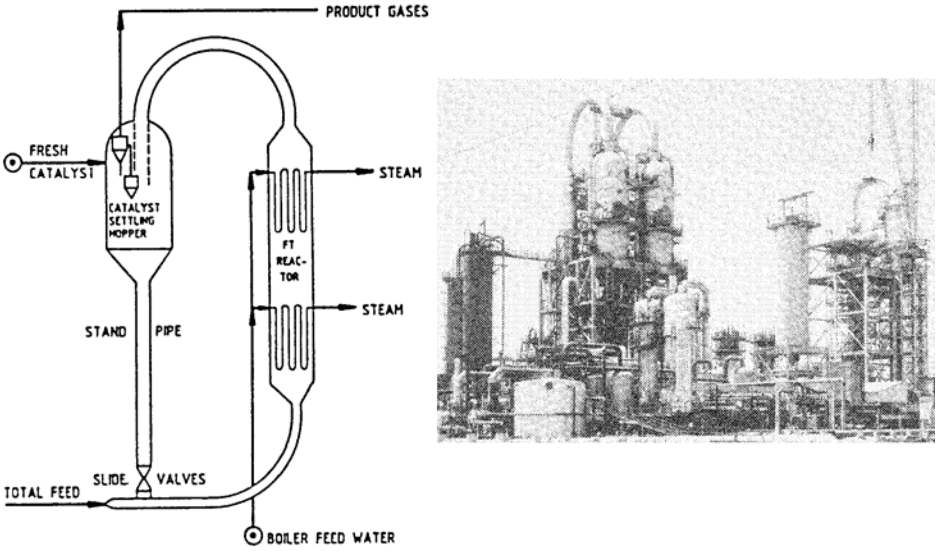

Figure 8. Kellogg circulating fluidised bed (CFB) reactors at Sasol 1. (These figures have been reproduced directly from Refs.(37) and (35), and are copyright protected).

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[s] On 26 September 1950 the "Suid-Afrikaanse Steenkool, Olie- en Gaskorporasie Beperk" became a public company, with Dr. P. E. Rousseau as managing director.

[t] The Kellogg HTFT section was commissioned on 23 August 1955 and the Arge LTFT section on 26 September of the same year. By 1 November 1955 the refinery already produced petrol for the local market.

[u] The HTFT circulating fluidised bed (CFB) reactor technology that was installed in Sasol 1 will be referred to as "Kellogg" to differentiate it from the modified "Synthol" CFB reactor technology developed by Sasol in the 1970's. It should be noted that the word "Synthol" has been in colloquial use since the 1940's. Ref.(2)

Kellogg and had only been tested on a 0.1 m diameter pilot plant scale. This design was scaled up to 2.3 m diameter, 46 m high units for use at the Sasol 1 facility(19)(38)(39) and each Kellogg reactor had a designed production capacity of 2000 bpd.(40) Typical operating conditions proposed by Kellogg for Fischer-Tropsch synthesis were 290-340°C and 1.9 MPa.(41) One of the design advantages cited for the use of a CFB reactor was the ability to change catalyst while the unit is in production.[v],(41) Although this was the design intent, the Kellogg reactor technology did not live up to this promise and the operating procedure was eventually changed to campaign mode operation to make the technology work.(35) The run length was limited by carbon build-up on the catalyst and each run lasted about 50 days before the reactor had to be unloaded, cleaned and fresh catalyst was loaded.(42) This placed a serious constraint on equipment availability and in 1960 a third CFB reactor was installed.

Although the Kellogg CFB reactors proved to be flexible in terms of dealing with fluctuations in flow rate, composition, temperature and pressure of the synthesis gas, the design had serious operational difficulties associated with the catalyst circulation rate. There was a small operating window that allowed stable performance. At high catalyst flow rates the intercooler tubes of the reactor were plugged, resulting in a loss of heat transfer and increased erosion in the tubes that were not plugged. At low catalyst flow rates bridging of the catalyst in the standpipe occurred, causing an interruption in production.(43)

The process used a fused iron catalyst made from a magnetite ore (Allenwood ore),(44) similar to that for Hydrocol. However, the Hydrocol operation was a fixed fluidised bed, not a CFB and the fused catalyst supplied by Kellogg was not without its own problems.(35) During CFB operation the catalyst is turbulently transported at linear velocities of several meters per second. The mechanical strength of the catalyst is therefore of paramount importance. If the catalyst is not robust enough, catalyst attrition will result in excessive fines formation that would cause increased catalyst loss, as well as a change in the fluidisation behaviour.(42)(45)

The Sasol Research department was established in 1957 and spent much time in understanding the behaviour and requirements of fused iron Fischer-Tropsch catalysts. The suitability of local sources of magnetite was investigated and mill scale from the nearby Vanderbijlpark Iscor steelworks was used to replace the imported Allenwood ore. The preparation of fused iron catalyst and the influence of chemical promoters (e.g. K_2O) and structural promoters (e.g. MgO, Al_2O_3) have been described in literature.(38)(42)(44) After

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[v] The catalyst recirculation rate was estimated at more than 4000 $t \cdot h^{-1}$, with a loss due to fines of about 0.0015%.

production and milling of the catalyst to the correct particle size distribution, it is reduced with hydrogen in a fixed bed reactor at 350-450°C over a period of 2 days. The unreduced catalyst has a surface area of only 1 $m^2 \cdot g^{-1}$, but on reduction this could be increased from 2 to 30 $m^2 \cdot g^{-1}$, depending on the type of promoters that were used.

The product distribution from the Kellogg HTFT synthesis is given in Table 7.(46) When this is expressed in terms of only C_3+ hydrocarbons, it amounts to 32% C_3-C_4 LPG, 53% naphtha, 8% diesel and 7% residue. As expected, the Kellogg syncrude is very similar to that of Hydrocol syncrude (Table 4). The product is quite olefinic and being an HTFT technology, the syncrude contains aromatics too (Table 8).(46) The oxygenates partition between the aqueous and organic product phases. Most of the lighter oxygenates end up in the aqueous product and are classified as either non-acid chemicals, or as carboxylic acids (Table 9).(40) The non-acid chemicals are typically aldehydes, ketones and alcohols. It should be noted that the product composition in Table 7 is not exactly the same as that obtained with present fused iron catalysts.[w]

Table 7. Fischer-Tropsch syncrude composition from the Sasol 1 HTFT Kellogg circulating fluidised bed reactors.

Compound	Mass %
Methane	10
Ethylene	4
Ethane	6
Propylene	12
Propane	2
Butenes	8
Butanes	1
C_5-C_{12}	39
C_{13}-C_{18}	5
C_{19}-C_{21}	1
C_{22}-C_{30}	3
C_{31} and heavier products	2
Non-acid chemicals	6
Carboxylic acids	1

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[w] The Kellogg CFB reactors at Sasol 1 has been decommissioned in the 1990's, but fused iron catalysts are used in the more modern versions of this technology too.

Table 8. Compound classes in Kellogg HTFT syncrude.

Product fraction	Paraffins (%) [‡]	Olefins (%)	Aromatics (%)	Alcohols (%)	Carbonyls (%)
C_5-C_{10}	13	70	5	6	6
C_{11}-C_{14}	15	60	15	5	5

[‡] The *n*-paraffin content of the paraffin fractions are 55% (C_5-C_{10}) and 60% (C_{11}-C_{14}).

Table 9. Non acid chemicals and carboxylic acids in the aqueous product of Kellogg HTFT synthesis.

Compound	Mass %
Non-acid chemicals [‡]	
Methanol	1.4
Ethanol	55.6
1-Propanol	12.8
2-Propanol	3.0
1-Butanol	4.2
2-Butanol	0.8
2-Methylpropanol	4.2
1-Pentanol	1.2
2-Pentanol	0.1
Other alcohols	0.6
Acetaldehyde	3.0
Propionaldehyde	1.0
Butyraldehyde	0.6
Pentanal	0.2
Acetone	10.6
Butanone (MEK)	3.0
Pentanones	0.8
Carboxylic acids	
Acetic acid	70
Propionic acid	16
Butyric acid	9
Other acids	5

[‡] The non-acid chemical composition in the source document does not add up to 100%.

4.2. Arge Fischer-Tropsch synthesis

The Arge LTFT design used a precipitated iron catalyst and synthesis is performed in a multi-tubular fixed bed reactor (Figure 9). Five Arge reactors were installed in the Sasol 1 plant with a design capacity of 550 bpd per reactor.x,(40) Every Arge reactor contains 2052 tubes and each tube is 12 m long with a 50 mm internal diameter.(41)(47)(48) The reaction temperature is controlled and maintained almost isothermally by regulating the pressure at which the boiler feed-water is allowed to evaporate on the outside of the reactor tubes. Typical operating conditions of Fischer-Tropsch synthesis during start up are 200-230°C and a gas inlet pressure of 2.5-2.7 MPa. During operation the temperature is increased by 25-30°C before end-of-run conditions is reached.(41) The process has been designed to use a H_2:CO ratio of 1.7-1.8:1.(41)

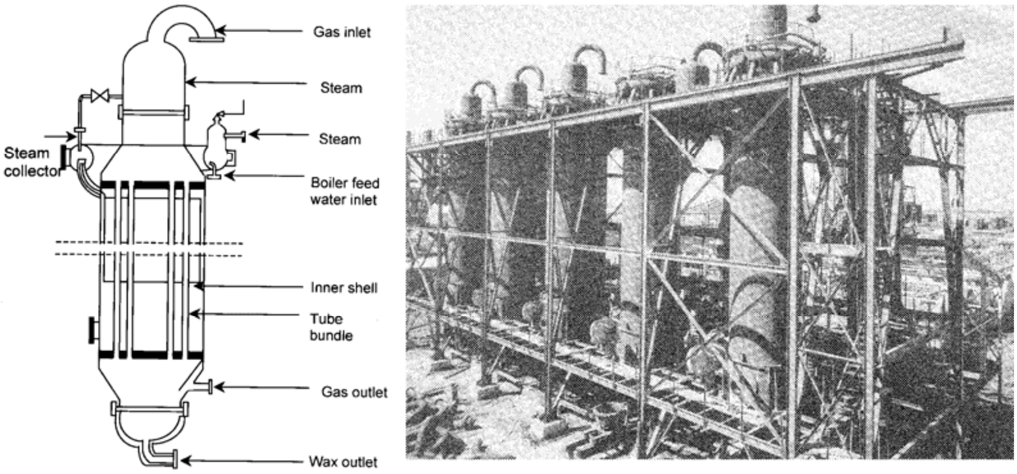

Figure 9. Arge multi-tubular fixed bed reactors at Sasol 1. (These figures have been reproduced directly from Refs.(19) and (35), and are copyright protected).

The precipitated iron catalyst is produced on site by dissolving iron in nitric acid and precipitating it by adding sodium carbonate. The potassium promoter is added before drying and extrusion to produce extrudates (about 3 mm diameter and 10 mm long). The catalyst is reduced at around 220°C and is coated in wax to prevent re-oxidation before being loaded in the reactor. Commissioning of the reactor is conducted under a hydrogen atmosphere to prevent the formation of iron carbonyl, which is volatile.(44)

The Arge LTFT syncrude composition (Table 10)(46) is typical of a high α-value Fischer-Tropsch product. The product contains less olefins and no aromatics, because it is

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[x] Arge reactor production capacity is approximately 18 000 tons per year per reactor. Ref.(40)

LTFT technology (Table 11).(46) The oxygenates are rich in alcohols, with little carboxylic acids and ketones being produced, as is expected from low temperature operation. Although the Arge reactors at Sasol 1 are still in production, the catalyst has been improved over the years and the precipitated iron catalyst presently used has a higher α-value.

Table 10. Syncrude composition from Arge LTFT synthesis.

Compound	Mass %
Methane	5
Ethylene	0.2
Ethane	2.4
Propylene	2
Propane	2.8
Butenes	3
Butanes	2.2
C_5-C_{12}	22.5
C_{13}-C_{18}	15
C_{19}-C_{21}	6
C_{22}-C_{30} (medium wax)	17
C_{31} and heavier products (hard wax)	18
Non-acid chemicals	3.5
Carboxylic acids	0.4

Table 11. Compound classes in Arge LTFT syncrude.

Product fraction	Paraffins (%) ‡	Olefins (%)	Aromatics (%)	Alcohols (%)	Carbonyls (%)
C_5-C_{12}	53	40	0	6	1
C_{13}-C_{18}	65	28	0	6	1

‡ The *n*-paraffin content of the paraffin fractions are 95% (C_5-C_{12}) and 93% (C_{13}-C_{18}).

4.3. Sasol 1 gas loop

The Sasol 1 plant has been designed to use coal as feed material. The coal is gasified in nine Lurgi high-pressure moving bed gasifiers in the presence of oxygen and steam. The temperature is kept low enough to prevent the ash from fusing to form clinker(49) and the gasifiers were designed to operate with coal having a high ash content.[y] The gasifiers were operated in the range 700-850°C reaction temperature, 300-650°C product gas outlet temperature and 2-3 MPa pressure.(50) When the Sasol 1 gasifiers were built, they were the largest in the world. To distinguish the original design from improved versions, these gasifiers were called Lurgi Mark I gasifiers.[z]

In terms of gasifier design it would be an over-simplification to classify gasifiers only by operating temperature, but in terms of refining this is a useful classification. The main difference from a refining perspective between low and high temperature gasification is that low temperature gasifiers, like those installed at Sasol 1, co-produces coal pyrolysis products with the raw synthesis gas. These products must be separated from the raw synthesis gas (Figure 10).(50) Separation of the neutral oil, gas liquor and tar is based on liquid density differences. The liquid product also contains dissolved light hydrocarbons, ammonia and carbon dioxide. The de-gassed coal pyrolysis product is rich in aromatics, phenols, tar acids and creosotes and can be refined to produce fuels and chemicals.

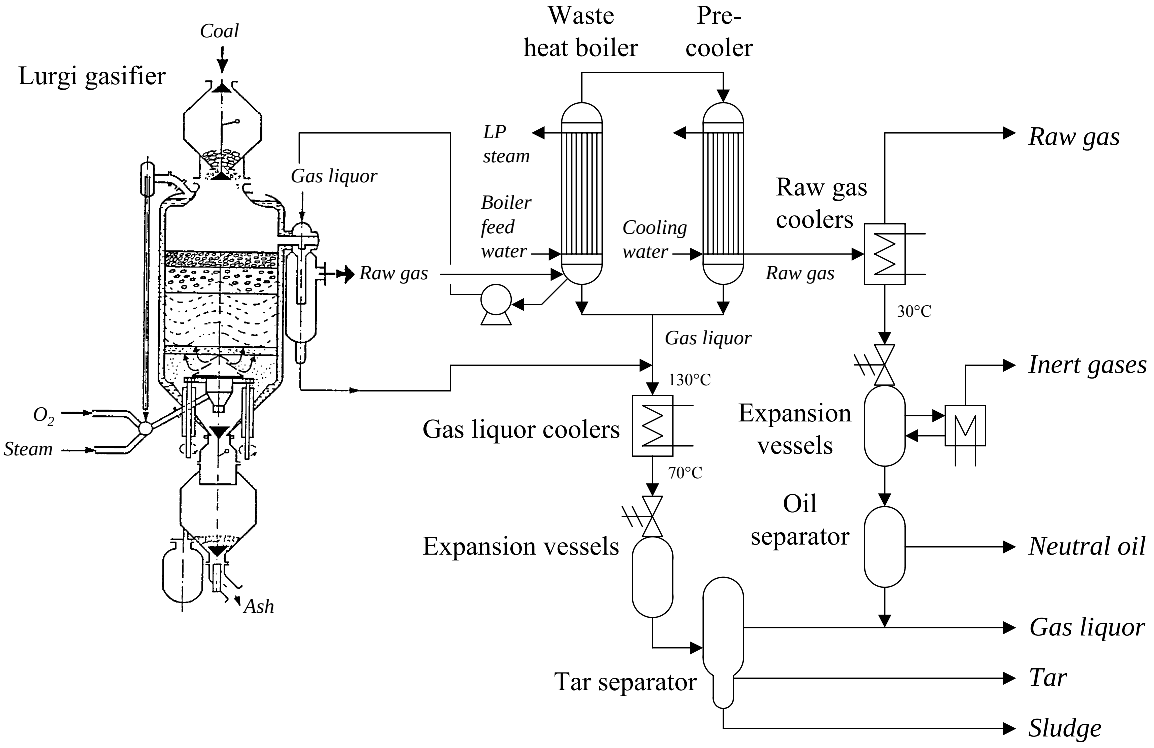

Figure 10. Low temperature Lurgi gasification and coal pyrolysis product separation at Sasol 1.

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[y] Coal samples from Coalbrook with an ash content of 30% were successfully tested in Germany in 1951 using Lurgi gasifiers.

[z] After commissioning of the gasifiers, only 80% of the design capacity could be achieved. Design capacity on the Lurgi Mark I gasifiers were only achieved at the end of 1957, while unit availability was only 78% (design unit availability was 89%).

The raw gas contains the synthesis gas components, CO and H_2, as well as significant quantities of methane, CO_2, H_2S and N_2 (the oxygen plant delivered O_2 at 99.1% purity to the gasifiers).(49) Since H_2S and organic sulphur containing compounds are Fischer-Tropsch catalyst poisons, these compounds had to be removed from the raw gas. This was done in a Rectisol unit, which uses methanol under pressure at cryogenic conditions to remove all sulphur containing compounds, in addition to removing about 98% of the CO_2.(49) The Rectisol process consists of three steps (Figure 11):(51) a) a pre-wash that removes hydrocarbons, oxygenates and organic sulphur compounds from the gas; b) a main wash that liquefies the CO_2 and removes most of the COS and CS_2 in addition to 95% of the CO_2; and c) a fine wash that removes the remaining sulphur components (COS and H_2S) in addition to some further CO_2 removal. The pure gas that contains at most 0.04 $mg\cdot m_n^{-3}$ sulphur, is then sent to the Fischer-Tropsch synthesis reactors. The Rectisol process was a new process in 1955(52) and the unit at Sasol 1 was the first commercial installation. It consisted of three identical scrubbing trains followed by a common regeneration section.(49) A more detailed description of the Rectisol process can be found elsewhere.(53)(54)

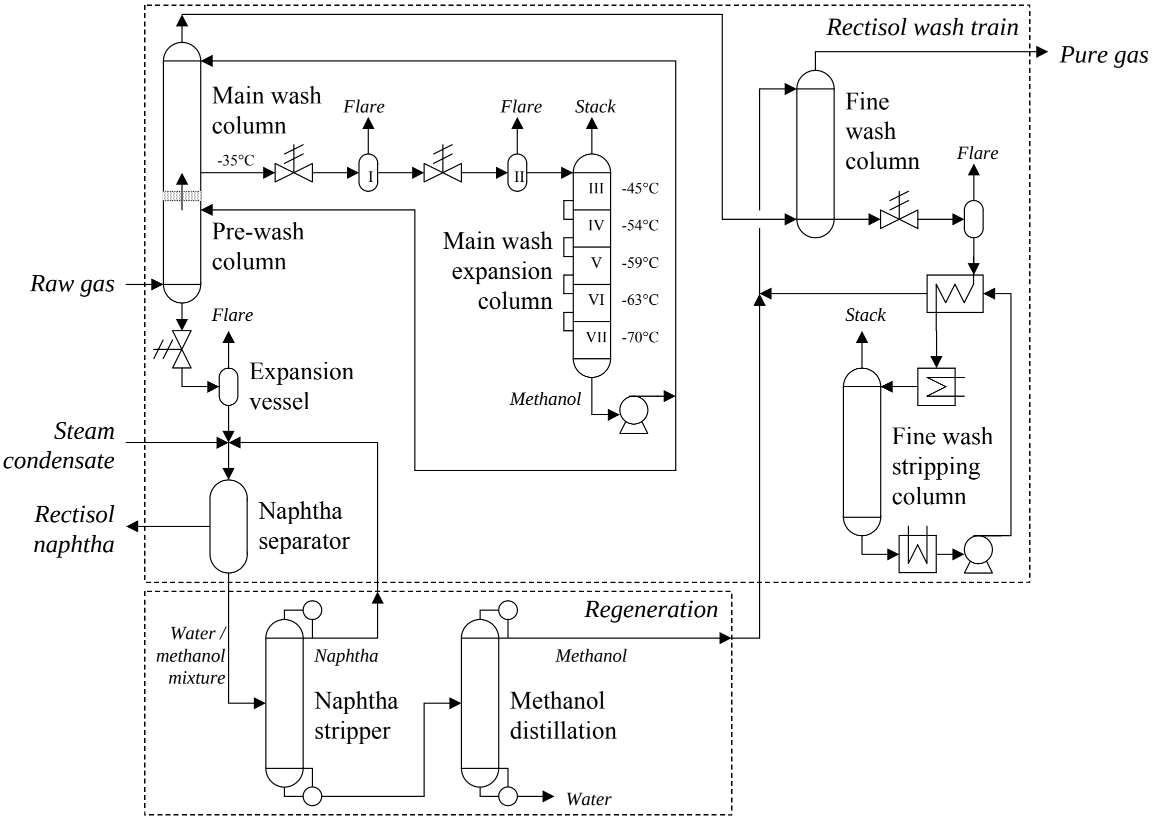

Figure 11. Rectisol process flow diagram.

The original Sasol 1 gas loop design is especially interesting, because it combined LTFT and HTFT synthesis reactors operating at different temperatures and pressures, with different H_2:CO ratios into a single gas loop (Figure 12).(41)(49) The Arge LTFT reactors required a higher pressure and had lower synthesis gas conversion than the Kellogg HTFT reactors. The tail gas from Arge synthesis was partly recycled to the Arge reactors to ensure the correct H_2:CO ratio (LTFT internal recycle), and partly sent to the gas reformer in the HTFT gas loop to convert the methane to synthesis gas and increase overall conversion. The tail gas from Kellogg synthesis was partly recycled to the Kellogg reactors (HTFT internal recycle) and partly sent to the gas reformer (HTFT external recycle). In this way the high CO conversion during HTFT synthesis was used to convert the unreacted CO from LTFT synthesis.

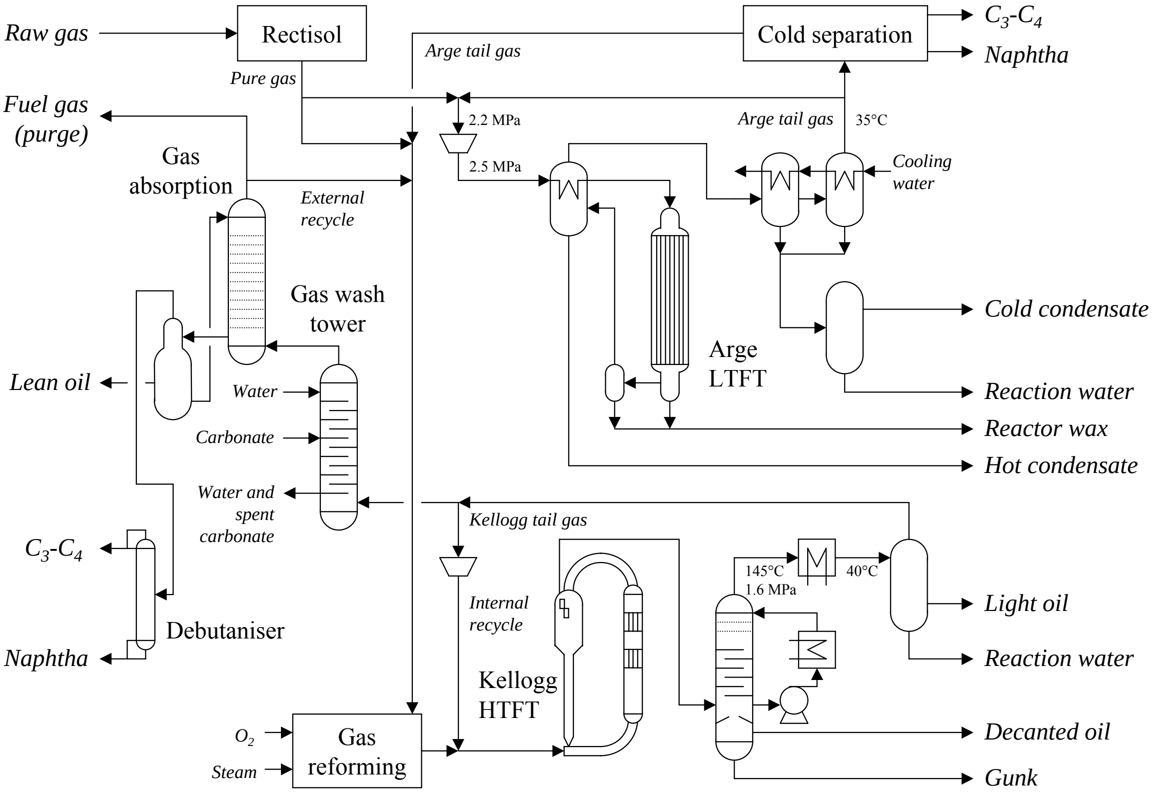

Figure 12. The Sasol 1 gas loop.

The flowscheme of the original Sasol 1 gas loop is clearly very complex. The feed material being sent to the refinery originates from gasification (coal pyrolysis products), Rectisol (aromatic naphtha) and the two types of syncrude produced during HTFT and LTFT synthesis.

4.4. Sasol 1 refinery

The original Sasol 1 refinery consisted of four different refineries, namely tar work-up, Kellogg oil work-up, Arge oil work-up and chemical work-up (Figure 13). Tar work-up refined the products from low temperature coal pyrolysis that were separated from the raw synthesis gas in the gasification section, as well as during gas purification in Rectisol. Such a tar refinery can also be found in coking plants or any other process that involves coal pyrolysis.[aa] The tar work-up section is consequently not really part of the Fischer-Tropsch refinery, but a by-product of the gasification technology that was selected. Upgrading of coal liquids is a specialised topic in its own right(55) and will only be superficially treated for the sake of completeness.

The Kellogg, Arge and chemical work-up sections together constitute the Fischer-Tropsch refinery. It is interesting that the design had very little refinery integration, apart from common aqueous product work-up and transfer of the C_3-C_4 fraction from Arge oil work-up to Kellogg oil work-up. This is in marked contrast to the approach that was followed during the gas loop integration.

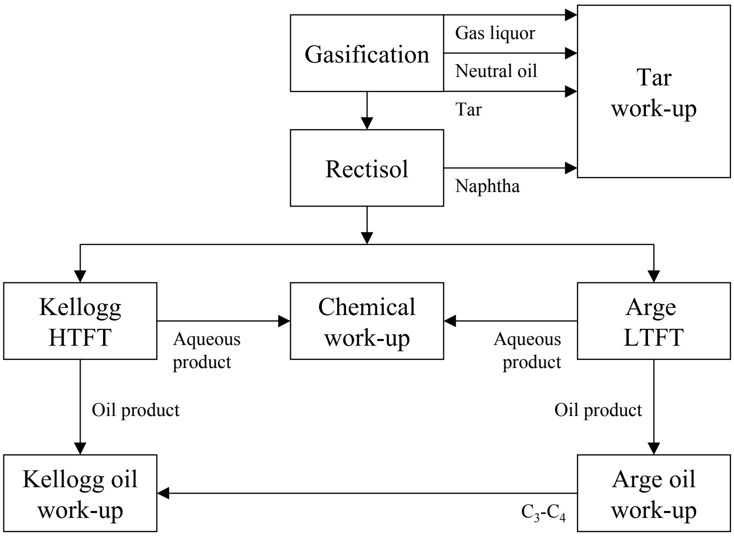

Figure 13. Sasol 1 refinery showing the feed origin for the various work-up sections.

[aa] Steel manufacturers may also have an associated tar refinery to work-up the products from their coking plant. Refining of these products has much more in common with direct coal liquefaction than with Fischer-Tropsch.

4.4.1. Sasol 1 tar work-up

The coal pyrolysis products are rich in aromatic and phenolic material. The basic Sasol 1 tar refinery flowscheme is shown in Figure 14. The gas liquor had an average concentration of 0.85% dissolved ammonia and 0.18% tar acids (phenolics). In the Phenosolvan process, the phenolic material is selectively extracted with butyl acetate at a pH of 8.5 to produce a crude phenol containing 40% phenol, 30% cresols, 7% xylenols and 23% higher boiling tar acids.(56) The ammonia was steam stripped from the phenol-lean gas liquor and converted into ammonium sulphate fertiliser.

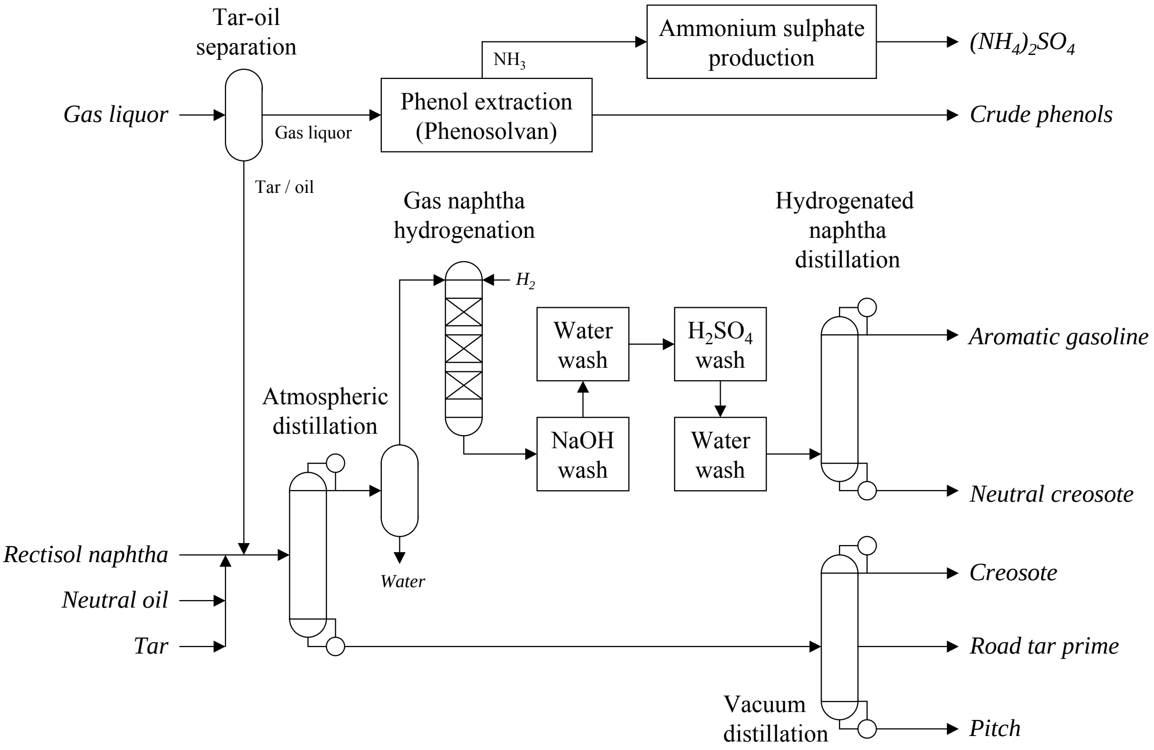

Figure 14. Sasol 1 tar work-up section.

The naphtha fraction from distillation of the Rectisol naphtha, neutral oil and tar, has been hydrogenated in a fixed bed reactor at 315-370°C and 5 MPa to remove gum forming substances and phenols, as well as to removed sulphur as H_2S. The hydrogenated product is cleaned by alkali and acid washing, before being distilled. Although only the fractionation scheme for aromatic motor-gasoline has been shown, the hydrogenated naphtha can also be fractionated in benzene, toluene, xylene, neutral oil and heavy naphtha fractions for the solvent market.(56) Most products from the tar refinery can in principle be sold as chemicals.

4.4.2. Sasol 1 Kellogg oil work-up

The HTFT Kellogg product refinery consisted of two conversion units, namely a clay-treater and a catalytic polymerisation unit (Figure 15).(57) The clay-treater used a silica-alumina acid-catalyst[bb] operated at 425°C to remove oxygenates and to improve the octane number of the α-olefin rich Kellogg syncrude by double bond isomerisation. In this respect it has a very similar function to the Bauxite treatment unit used in the Hydrocol process, but due to the more acidic nature of the catalyst and higher operating temperature, it also resulted in catalytic cracking of the feed. The clay-treater produced cracked gas that was routed to the feed from the gas absorber with the product from the gas wash tower (Figure 12), where the C_3-C_4 fraction was recovered and returned to the Kellogg work-up section.

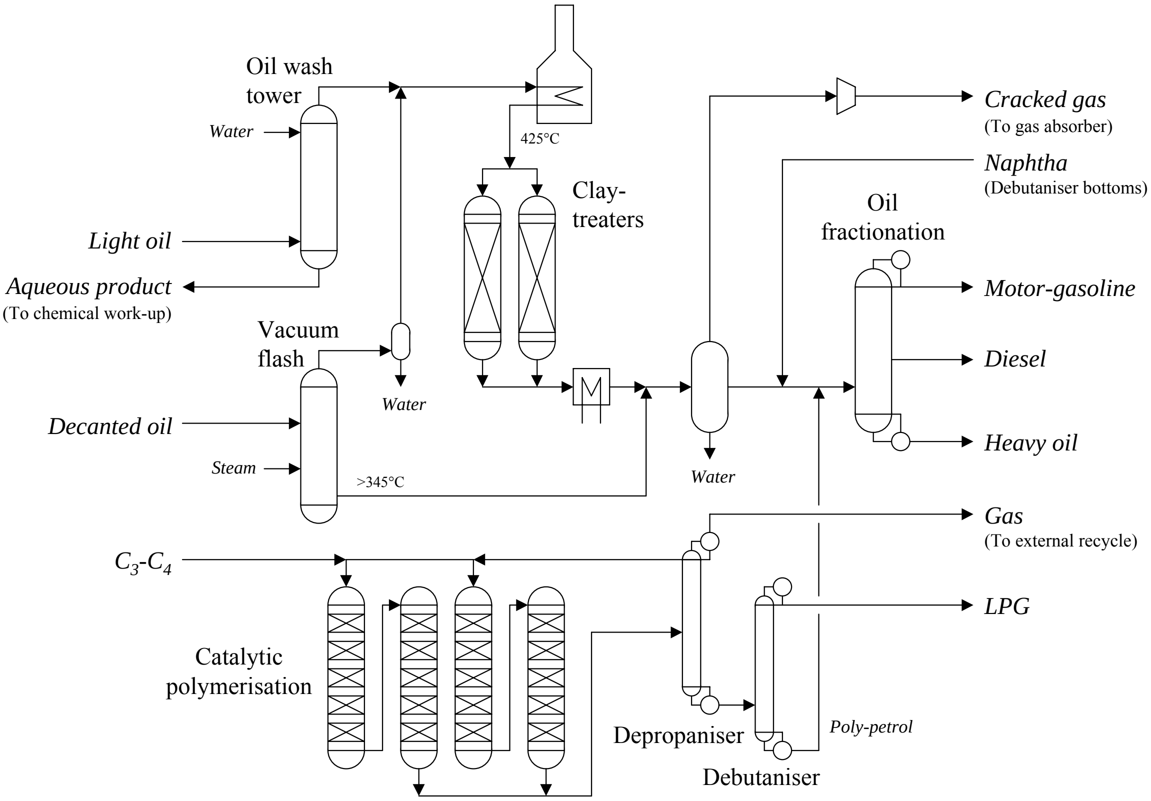

Figure 15. Sasol 1 Kellogg work-up section.

All C_3-C_4 molecules in the Sasol 1 plant were routed to the catalytic polymerisation unit, which oligomerised the gas that contained 60-70% olefins to produce a high octane olefinic motor-gasoline and some distillate. The olefin lean product gas (propane and butane rich) was used as fuel gas in the factory or sold as LPG. The oligomerisation technology

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[bb] The acidic clay was likely to be acidified montmorillonite, $H_x.aH_2O(Al_{4-x},Mg_x)^{oct}(Si_8)^{tet}O_{20}(OH)_4$, or beidellite, $H_x.aH_2O(Al_4)^{oct}(Si_{8-x}Al_x)^{tet}O_{20}(OH)_4$, which are naturally occurring zeolites. Ref.(58)

originally selected for the Sasol 1 refinery was that of the Polymer Corporation, which employed a copper pyrophosphate and charcoal catalyst.[cc],(59)(60)(61)(62) There were four reactors, each 1.2 m in diameter and 7.6 m high, containing five catalyst beds with inter-stage quench capability.[dd] Part of the feed was compressed to 6-7 MPa and pre-heated to 220°C before being introduced to the reactors, while the remainder of the feed was used as reactive inter-stage quenches. The reactors were configured to operate as a pair of two reactors in series. When fresh catalyst was loaded in one of the reactors, the reactor with fresh catalyst was always configured to be the second reactor in series to boost conversion, but prevent temperature excursions.(57)

The bottom product from the two debutaniser columns (Figures 12 and 15), the steam stripped decanted oil and the de-gassed product from clay-treatment were combined and used as feed to the oil fractionator. This produced motor-gasoline, diesel and fuel oil cuts as final products.

4.4.3. Sasol 1 Arge oil work-up

There are three conversion units in the Arge work-up section, namely Bauxite treatment, catalytic cracking and wax hydrogenation (Figure 16).(57) Bauxite treatment, which is similar to that used in the Hydrocol refinery, converts the oxygenates and double bond isomerises the olefins to produce a higher octane motor-gasoline as final product. The feed is obtained from the Arge tail gas, which is purified in the gas loop to remove the light hydrocarbons (Figure 12). Only the C_5-C_7 fraction is converted over the Bauxite, because that is the only fraction where the final product had a high enough octane number to be used as final product. The process was operated at 400°C, slightly lower than the clay-treaters in the Kellogg work-up, but the aim of both processes were the same. The reason for having a separate Bauxite treatment unit in Arge work-up and not routing it to the Kellogg work-up, like the C_3-C_4 stream, is not clear.

The Paraformer, or paraffin reformer plant, is a thermal cracker that converts the hard wax to medium and soft wax, as well as the waxy oil fractions to diesel and motor-gasoline.(57) The conversion and product selectivity is controlled by varying the temperature, which is typically above 500°C.(63) The C_3-C_4 gas is sent to Kellogg work-up, while the

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[cc] This was probably done because Kellogg introduced a process based on this type of catalyst. Ref.(9)

[dd] This reactor design is very similar to that used for the UOP CatPoly and cumene processes that employ a solid phosphoric acid catalyst.

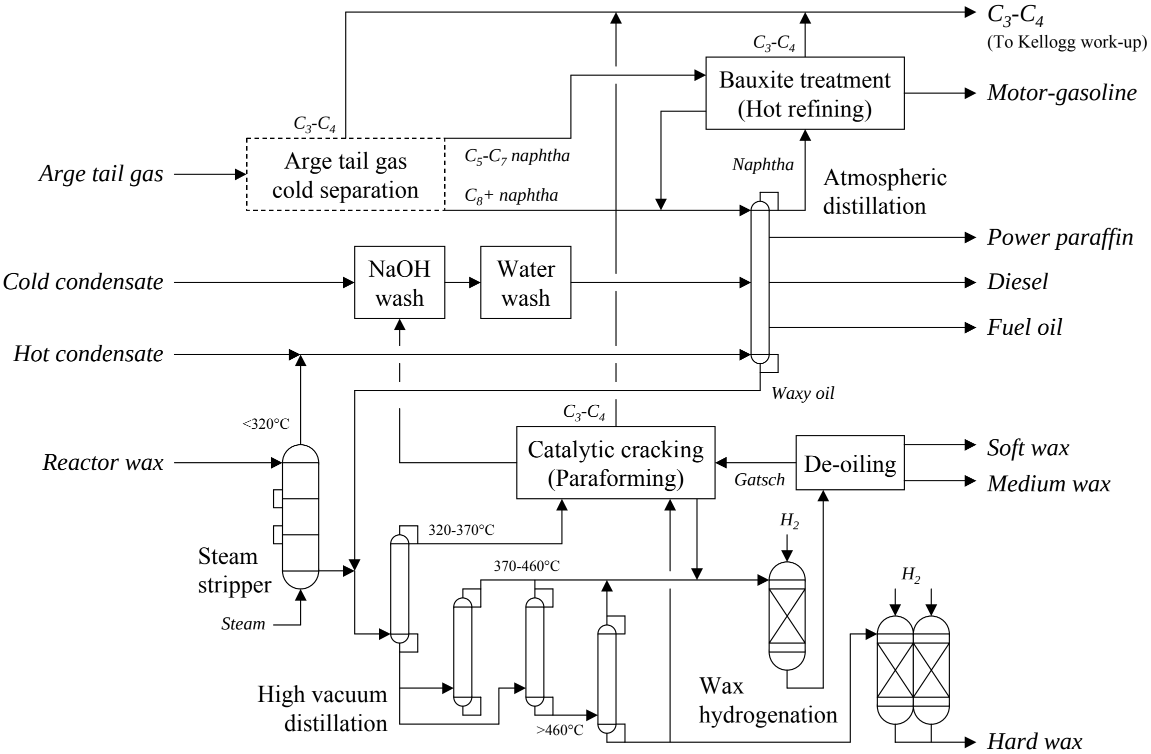

Figure 16. Sasol 1 Arge work-up section.

naphtha and distillate range product is caustic washed with the cold condensate before being distilled with the hot condensate into naphtha, power paraffin (kerosene), diesel, fuel oil and waxy oil fractions. The kerosene, diesel and fuel oil are final products, while the naphtha is first Bauxite treated before becoming motor-gasoline as final product.

Waxy oil and reactor wax are steam stripped to remove the lighter than 320°C material, before it is deep vacuum distilled to produce soft, medium and hard wax fractions. The waxes contain small amounts of olefins and oxygenates that has to be removed by hydrogenation. Hydrogenation was done at 260°C, 5 MPa and LHSV of 0.3-0.5 h^{-1}.[ee] Three reactors were used, two for hard wax hydrogenation and one reactor to hydrogenate the lighter fractions.(57)

The de-oiling of the wax was done by dissolving the wax in a suitable solvent at 60°C and then slowly cooling it down in a scraper cooler.(57) The wax fractions that crystallised could be recovered by filtration. Details of solvent dewaxing, which is typically performed with methyl ethyl ketone as solvent, can be found in literature.(65)

[ee] Although the catalyst type has not been specified in literature, it is stated that it is a "highly-active" catalyst. It is likely that it was an unsulphided nickel hydrogenation catalyst. For background on Fischer-Tropch wax hydrogenation see ref.(64).

4.4.4. Sasol 1 chemical work-up

The aqueous product from both Kellogg and Arge synthesis reactions contained about 6% oxygenates dissolved in the reaction water and was refined in the chemical work-up section (Figure 17).(57) The chemical work-up section consisted of two parts, chemical recovery and solvent recovery.

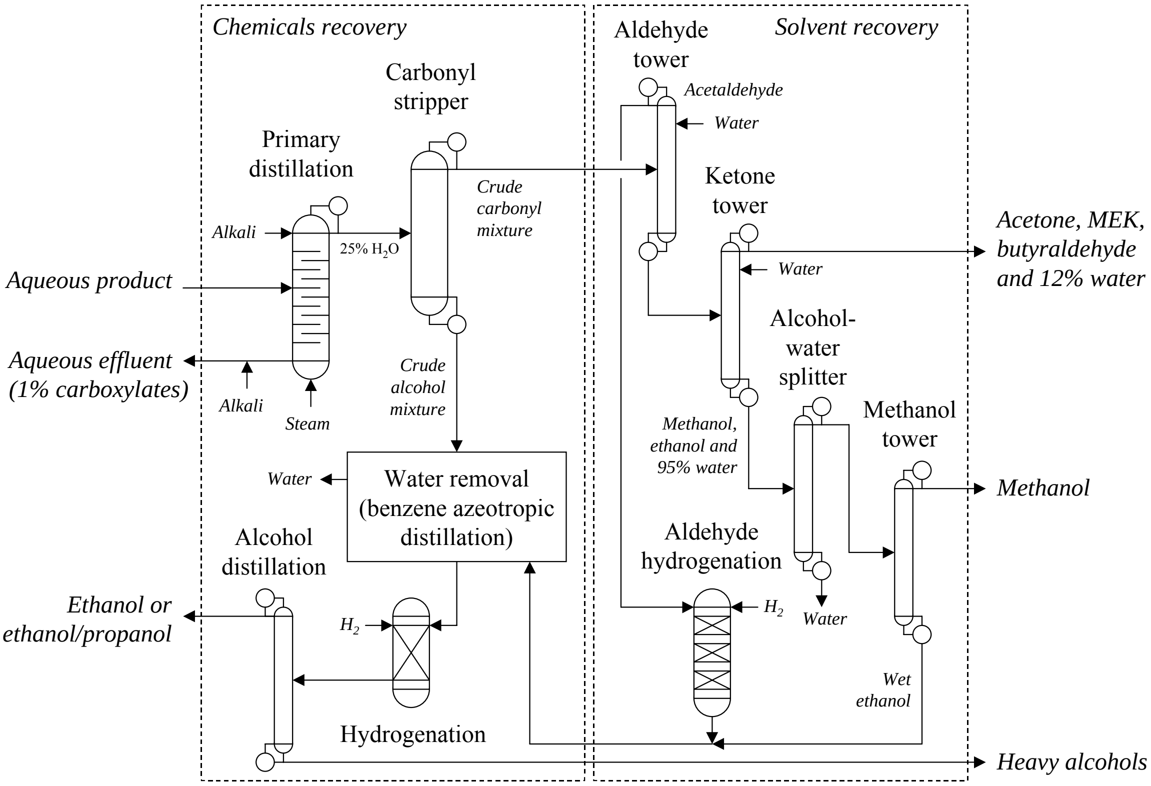

Figure 17. Sasol 1 chemical work-up section.

The aqueous product was first distilled in the primary distillation column, which was stainless steel lined on account of the carboxylic acids in the feed. To prevent any carboxylic acids from distilling into the overheads product, an alkali solution was injected on two trays near the top of the column. The bottoms product from the column was also treated with alkali to neutralise the carboxylic acids (Equation 1).

$$\mathrm{NaOH\ (aq) + RCOOH\ (aq) \rightarrow RCOONa\ (aq) + H_2O} \qquad \text{... (1)}$$

The overheads product from primary distillation was rich in oxygenates and contained 25% water. The carbonyl stripper was used to effect a crude separation between the alcohols and carbonyls. The overheads product contained mostly carbonyls (aldehydes and ketones), esters and methanol, while the bottoms product contained mostly water, ethanol and the heavier alcohols. The stripper overheads product was further refined in the solvent recovery section, while the alcohols were further purified in chemical recovery. The first step was water removal by azeotropic distillation with benzene, which is a textbook purification (Keyes process).(66) The water-free alcohol stream was then mildly hydrotreated to convert the residual aldehydes and ketones into alcohols. The final alcohol purification step was either used to produce ethanol or an ethanol-propanol mixture as fuel alcohols. The heavy alcohols were not enough to be purified by continuous distillation and the mixture was sent to the solvent recovery section where the alcohols were separated by batch distillation, which is not shown in Figure 17.

The overheads product from the carbonyl stripper was distilled in various steps to successively remove acetaldehyde, mixed carbonyls (mainly acetone, methyl ethyl ketone and butyraldehyde), water, methanol and ethanol. Of these, only methanol was a final product. The acetaldehyde was hydrogenated to ethanol at 150°C and 3.8 MPa over a nickel catalyst in a reactor with three catalyst beds and inter-stage quenching. It is interesting to note that preheating of the acetaldehyde was done in the presence of hydrogen, presumably to prevent aldol condensation reactions. The product was then combined with the wet ethanol from the methanol tower and processed with the other alcohols in the chemical recovery section. The mixed carbonyls, like the heavy alcohols, were further separated by batch distillation.

The aqueous effluent that contained about 1% carboxylates was concentrated in an evaporator to yield a 50% salt solution. The alkali was regenerated from this solution, but the acids were not recovered, although this intent was expressed.(56)

5. South African Sasol 2 and 3 technology (1970-1980's)

The Sasol 2 and 3 facilities are children of the 1973 oil crisis. The South African government requested Sasol on 30 November 1973 to investigate the technical and economic viability of building one or more coal-to-liquid facilities in the Republic of South Africa. The study was completed by early January 1974 and on 3 December 1974 the construction of Sasol 2 was publicly announced. In December 1978 the request was repeated and in January 1979 the government was provided with a report detailing the cost of doubling Sasol 2 (then still known as the Sasol 2 expansion project). In Iran the regime of the Shah was toppled and by February 1979 the decision to proceed with Sasol 3 was taken.(67)

Sasol 2 and 3 were grassroots facilities just like Sasol 1 and were erected about 100 km east of Johannesburg at the place presently called Secunda. Construction of Sasol 2 started in 1976 and commissioning of the steam plant took place early in 1979. In the same year, 1979, construction of Sasol 3 commenced. The synthesis and refining sections of Sasol 2 were commissioned in 1980,[ff] although the last Fischer-Tropsch Synthol-train was only commissioned in January 1981. Design production capacity of Sasol 2 was reached in 1982.

Commissioning of Sasol 3 took place in parallel with the start-up of Sasol 2 and already commenced in 1981, with the synthesis and refinery sections being commissioned in 1982.[gg] Design production capacity of Sasol 3 was reached on 16 February 1983.

The discussion of Sasol 2 and 3 will deal with the original designs. The design of the Sasol 2 and Sasol 3 refineries were similar, except for the addition of a high pressure creosote hydrogenation section (360 kta) to the tar refinery of Sasol 3, which processed creosote from both facilities.(67) Other minor improvements were also made to units based on lessons learnt from Sasol 2 and will be pointed out only where these led to significant differences between the Sasol 2 and Sasol 3 facilities.

5.1. Sasol Synthol Fischer-Tropsch synthesis

The Sasol HTFT Synthol reactor design is based on the Kellogg HTFT design used in the Sasol 1 facility. The circulating fluidised bed (CFB) design was optimised and many of the design problems of the original Kellogg reactors were sorted out.(43) The new CFB design was larger (7500 bpd)(42) and were operated at higher pressure. Typical operating conditions of the Synthol reactors were 330-360°C and 2.5 MPa.(39) A total of 16 Synthol reactors were installed at Secunda (8 Synthol reactors on each side), giving Sasol 2 and 3 a combined design production capacity of 120 000 bpd.

The same fused iron based Fischer-Tropsch catalyst as used for the Kellogg reactors were used for the Synthol reactors. With time the catalyst formulation has been improved as the effect of various promoters were better understood, although the basic formulation remained very similar. A typical product distribution from a commercial HTFT Synthol reactor is given in Table 12.(68)(69)(70)(71)

[ff] Sasol 2 produced its first hydrocarbon product on 1 March 1980 and marketable products were produced since 25 April 1980.

[gg] Sasol 3 produced its first hydrocarbons on 10 May 1982 and first marketable products by 1 July 1982.

The distribution of water soluble oxygenates are given in Table 13.[hh],(72)(73) It will be noted that slight variations are reported, which is expected, since it is known that the product spectrum is temperature dependent.(38) In many respects the composition of Synthol products (Tables 12-13) is similar to that of Kellogg products (Tables 7-9) as would have been expected, since the designs are very similar.

Table 12. Typical product distribution from HTFT Synthol operation.

Compound	Composition (mass %)			
	ref.(68)	ref.(69)	ref.(70)	ref.(71)
Methane	11	10	10	11
Ethylene	4	4	4	7.5
Ethane	3.4	4	3.5	
Propylene	11.4	12	12	13
Propane	1.4	2	2	
Butenes	9.3	9	9	11
Butanes	2	2	2	
C_5-C_6 olefins	12.8			
C_5-C_6 paraffins	2.6			
C_7-160°C	17.2	51	51.5	51.5
160-350°C	13			
>350°C	5.4			
Non-acid chemicals	6.5	5	6	6
Carboxylic acids		1		

[hh] This data in ref. (72) has been published before Sasol 2 was commissioned and is likely to be the pilot plant data used by Fluor for the design of Sasol 2.

Table 13. Oxygenates in the aqueous product of Synthol HTFT synthesis.

Compound	Composition (mass %)	
	ref.(72)	ref.(73)
Non-acid chemicals		
Methanol	1.2	0.9
Ethanol	46.4	49.7
1-Propanol	10.7	14.5
2-Propanol	2.5	
1-Butanol	3.5	6.3
2-Butanol	0.7	
2-Methylpropanol	3.5	
1-Pentanol	1.0	1.8
2-Pentanol	0.1	
Other alcohols	0.5	
Acetaldehyde	2.5	4.5
Propionaldehyde	0.8	
Other aldehydes	0.5	
Acetone	8.9	9.0
Butanone (MEK)	2.5	2.7
Pentanones	0.7	0.9
Other ketones	0.2	
Carboxylic acids		
Acetic acid	9.7	6.7
Propionic acid	2.2	1.5
Butyric acid	1.2	0.9
Other acids	0.7	0.5

5.2. Sasol 2 and 3 gas loops

Sasol 2 and 3 also used Lurgi gasifiers to convert coal with a high ash content into raw synthesis gas. Since the commissioning of the Sasol 1 plant, many improvements were made to the Lurgi gasifiers and by the time Sasol 2 was constructed, an improved Lurgi Mark IV test gasifier was already in operation at the Sasol 1 site.[ii] At total of 80 Lurgi Mark IV gasifiers were installed at Secunda, 40 per plant, each 3.85 m in diameter and able to processes about 1000 tons of coal per day, yielding 55 000 $m^3 \cdot h^{-1}$ (normal) raw synthesis gas.(45)(74)(75)

Since the Lurgi gasifiers are low temperature gasifiers, coal pyrolysis products are co-produced with the synthesis gas. The separation methodology followed to separate the raw synthesis gas from these pyrolysis products is very similar to that employed in the Sasol 1 design (Figure 10). It was only more involved, with additional coolers and tar separators forming part of the design (Figure 18).(76)

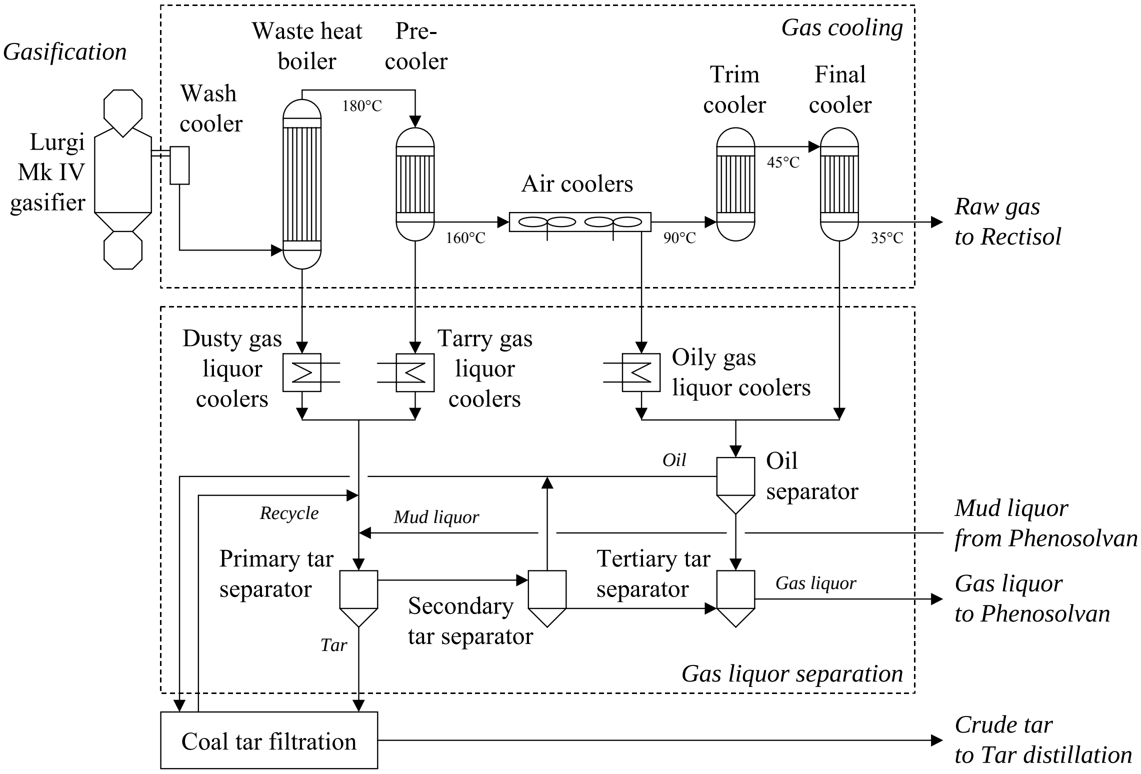

Figure 18. Sasol 2 and 3 gasification and coal pyrolysis product separation.

Purification of the raw gas to remove CO_2 and H_2S and produce pure synthesis gas, is done by a cold methanol wash in a Rectisol process.(53)(54) Due to the size of the Secunda facility, more than one Rectisol train have been built. The size of the Rectisol trains was limited by the maximum size of the vessels that could be transported by road.(74) Unlike the design of the Sasol 1 plant, in Sasol 2 and 3 the hydrogen sulphide from the Rectisol units is

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[ii] The commissioning of a Lurgi Mk IV gasifier in 1978 at Sasol 1 allowed sufficient time for optimisation and allowed the commissioning of these gasifiers at Sasol 2 to proceed without significant delay. Ref.(74)

recovered in a modified Stretford-type process, called Sulfolin.[jj] In Stretford process the hydrogen sulphide is absorbed in a sodium carbonate solution (Equation 2). In solution it is oxidised by vanadium(V) to produce elemental sulphur (Equation 3) that can be recovered. The vanadium(IV) formed during this step is converted back to vanadium(V) by reoxidation with air (Equation 4) to make the process catalytic.(77)(78)(79)

$$H_2S + Na_2CO_3\ (aq) \rightarrow NaHS\ (aq) + NaHCO_3\ (aq) \qquad \text{... (2)}$$

$$2\ NaSH\ (aq) + 4\ NaVO_3\ (aq) + H_2O \rightarrow Na_2V_4O_9\ (aq) + 4\ NaOH\ (aq) + 2\ S \downarrow \qquad \text{... (3)}$$

$$Na_2V_4O_9\ (aq) + 2\ NaOH\ (aq) + O_2 \rightarrow 4\ NaVO_3\ (aq) + H_2O \qquad \text{... (4)}$$

The pure gas from Rectisol is mixed with internal and external recycle streams to produce a feed with a H_2:CO of 1.7-2.0 for the Synthol reactors (Figure 19). The internal recycle consists of the tail gas produced after knocking out the products that could be condensed by water cooling. These condensed products are sent to the refinery. Hydrogen from the pressure swing absorption (PSA) unit and the products from methane reforming(80) with oxygen over a nickel catalyst are combined to constitute the external recycle. To enable the recovery of hydrogen and methane, the gas loop includes a cold box where these compounds can be cryogenically separated from the heavier hydrocarbons. The inclusion of a CO_2 removal step is essential, since CO_2 solidifies at the cryogenic conditions prevailing in the cold box. The CO_2 removal is done in a Benfield unit, which uses a hot potassium carbonate wash and the reversible acid-base reaction between the basic carbonate and carbonic acid formed by dissolved CO_2 (Equation 5).(81)(82)

$$CO_2 + H_2O + K_2CO_3\ (aq) \rightleftharpoons H_2CO_3\ (aq) + K_2CO_3\ (aq) \rightleftharpoons 2\ KHCO_3\ (aq) \qquad \text{... (5)}$$

The tails gas from Benfield is dried in an amine unit, which is then further dried by passing it over a mol sieve.(74) The cold box flow diagram shown in Figure 19 has been considerably simplified to avoid the complicated heat integration that is typically found in such units.(83) A large portion of the light products from HTFT synthesis is condensed in the cold box. With the exception of the C_2 and lighter products and some of the propylene, the rest of the hydrocarbons that are separated in the cold box are sent to the refinery as

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[jj] The first Stretford tower was built at Sasol 1 in 1973, but failed to work due to microbial growth in the water and the wrong type of wood used as packing material. These problems were overcome with the help of Linde and therefore the Secunda process was called Sulfolin, although it used basically the same chemistry. Ref.(75)

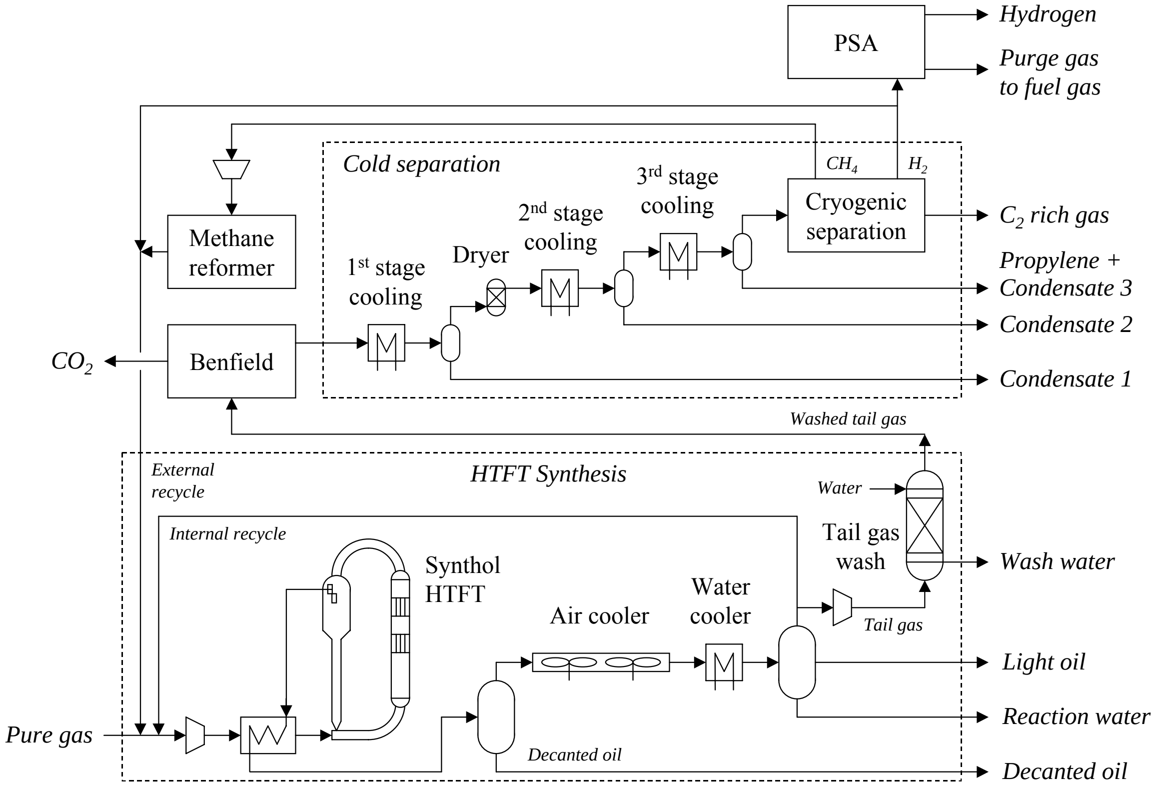

Figure 19. Sasol 2 and 3 original gas loop design (1980's).

Condensates 1, 2 and 3. Since the Condensate 1, 2 and 3 streams are produced by progressive cooling, the composition of Condensate 1 (C_3-C_7) is such that it contains heavier hydrocarbons than Condensate 2 (C_4-rich), which in turn contains heavier hydrocarbons than Condensate 3 (C_3-rich). The ethylene and some propylene are separated as pure compounds and are used as feed to produce polymers. The methane is recycled to the synthesis section where it is converted to synthesis gas in the methane reformer.

5.3. Sasol 2 and 3 refineries

The Sasol 2 and 3 refineries each consists of four different refineries (or value chains as they are called in Sasol), namely tar work-up, condensate work-up, oil work-up and chemical work-up (Figure 20). The plant organisation differs slightly from the Sasol 1 breakdown shown in Figure 13, because the Phenosolvan and Ammonia recovery units are seen as part of the gas production sections and not part of the tar refineries. A further difference is the organisational separation of condensate work-up and oil work-up, which in practise are very inter-linked, and will be discussed together.

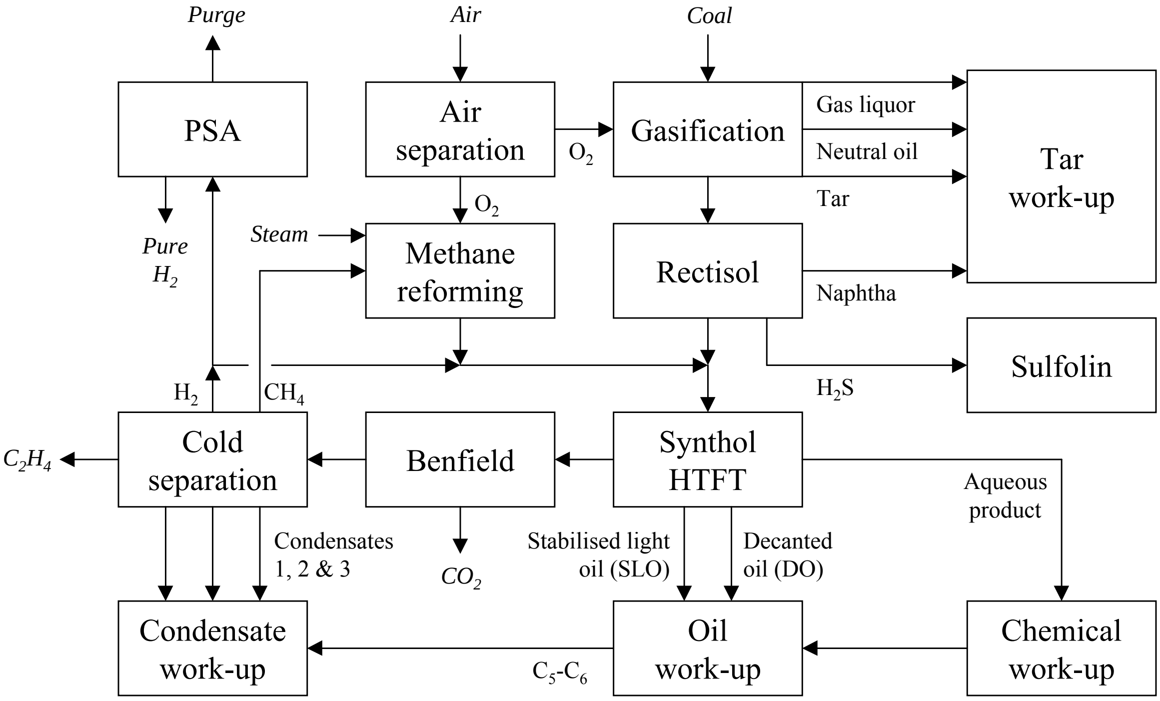

Figure 20. Block flow diagram of Sasol 2 and 3 showing the feed origin for the various work-up sections.

As noted during the discussion of the Sasol 1 refinery, the tar work-up section refines the products from low temperature coal pyrolysis that were separated from the raw synthesis gas and is strictly speaking not part of the Fischer-Tropsch refinery. A tar refinery will not be required if a high temperature coal gasification technology is used, or when natural gas is used as feed. Since the products from the tar refinery were blended with the Fischer-Tropsch derived synthetic fuels, it is an example of cross-platform integration.

Although it is not considered part of the refinery, it should be noted that both Sasol 2 and Sasol 3 included ammonia synthesis as part of their original design.(75) This makes sense, since large quantities of pure nitrogen is available from the air separation units (ASUs) as a by-product at essentially no additional cost. The manufacture of ammonia was extended to the production of nitrogen-based chemicals for the fertiliser (agricultural)[kk] and explosives (mining)[ll] industries.

[kk] Sasol entered the fertiliser industry in 1964 by adding ammonia synthesis to the Sasol 1 facility. However, things started going wrong in the 1980's when the Secunda fertiliser plant was added, since South Africa experienced its worst drought in 200 years. This was only a temporary setback.

[ll] The explosives business that was established in 1984, with a porous ammonium nitrate plant that was commissioned in Sasolburg in 1985 and a cartridge emulsion explosives plant that was commissioned in Secunda in the same year. Later an emulsion explosives plant was commissioned in the Northern Cape. The group posted a profit since 1989 and was renamed Sasol Mining Explosives (SMX).

5.3.1. Sasol 2 and 3 tar work-up

The recovery of phenolic material and ammonia by a Phenosolvan process, similar to that described for the Sasol 1 plant (section 4.4.1), also forms part of the Sasol 2 and 3 designs. The feed to the tar distillation unit consists of the phenolic pitch, after phenol extraction in the Phenosolvan unit, and crude tar from the coal tar filtration unit (Figure 21). These feeds are combined with a recycle stream from the coal tar naphtha hydrogenation unit before being distilled. A typical product distribution from tar distillation consists of six fractions, namely light naphtha (10%), heavy naphtha (8%), medium creosote (25%), heavy creosote (13%), residue oil (5%) and pitch (39%).(84)

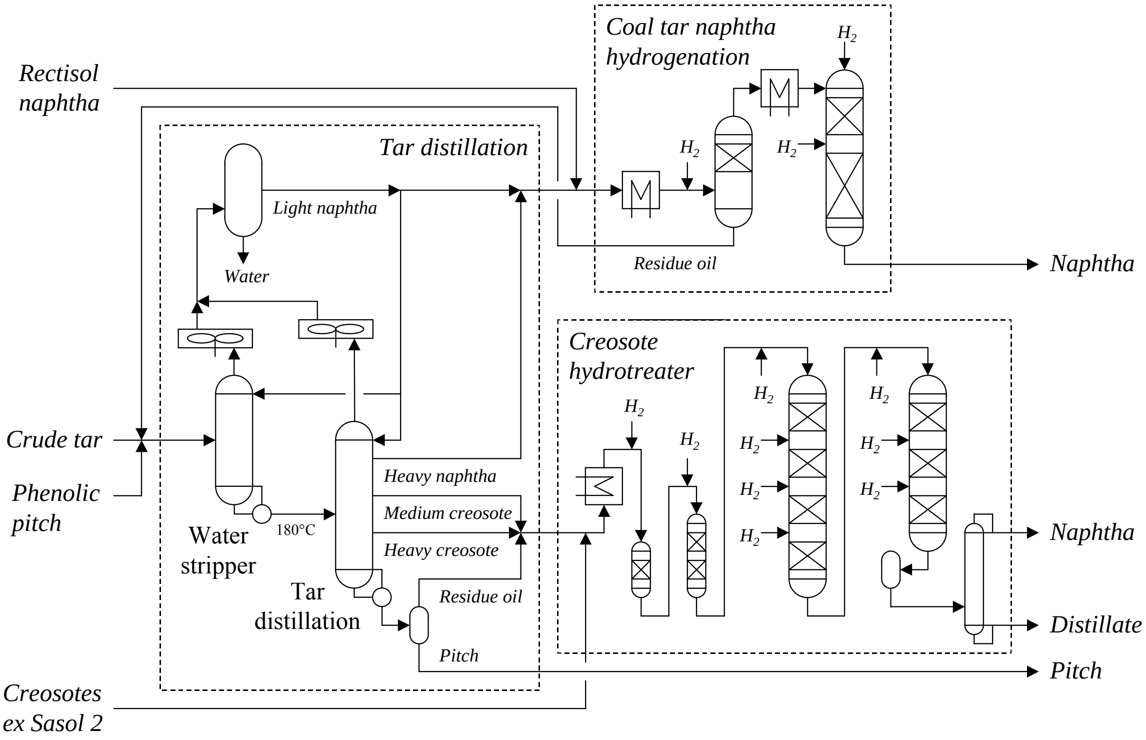

Figure 21. Sasol 3 tar work-up section. The tar work-up section of Sasol 2 is similar, but it does not contain a creosote hydrogenation unit.

The light naphtha, heavy naphtha and Rectisol naphtha from the Rectisol unit are combined to serve as feed for the Coal tar naphtha (CTN) hydrogenation unit. In this unit the feed is pre-heated and flashed to separate the naphtha range material from the heavier boiling material at around 210°C. The heavier material, called residue oil, is recycled to the tar distillation unit, while the naphtha vapour is hydrogenated at 5 MPa pressure. Separation of the heavier material takes place in the first reactor, which is operated in up-flow mode. This reactor is loaded with a mild hydrotreating catalyst and is mainly used for diene saturation.

Most of the hydrotreating is done in the second reactor that has two catalyst beds (originally a Co/Mo-Al_2O_3 catalyst) with an inter-stage hydrogen quench. The product is a hydrogenated naphtha consisting of mainly paraffins and aromatics, but with low octane number (typically around 80) and is used a fuel blending component. Most of the benzene in the fuel pool comes from this product.

The medium creosote, heavy creosote and residue oil from the tar distillation units at both Sasol 2 and Sasol 3 are combined and hydrogenated at high pressure (18 MPa) in the creosote hydrotreater at Sasol 3. The tar refinery at Sasol 2 does not have such a unit. The unit consists of four reactors with multiple catalyst beds and inter-stage hydrogen quenches. The catalysis of this unit is discussed in a recent paper.(85) The product is mixture of hydrogenated naphtha and distillate, which are used as fuel blending components. The creosote diesel is an especially important blending component, since it is the main source of diesel density in the refinery.

5.3.2. Sasol 2 and 3 condensate and oil work-up

The condensate and oil work-up sections are integrated (Figure 22). These were designed to meet the following objectives:(86) a) Convert normally gaseous C_3 and C_4 olefins to liquid

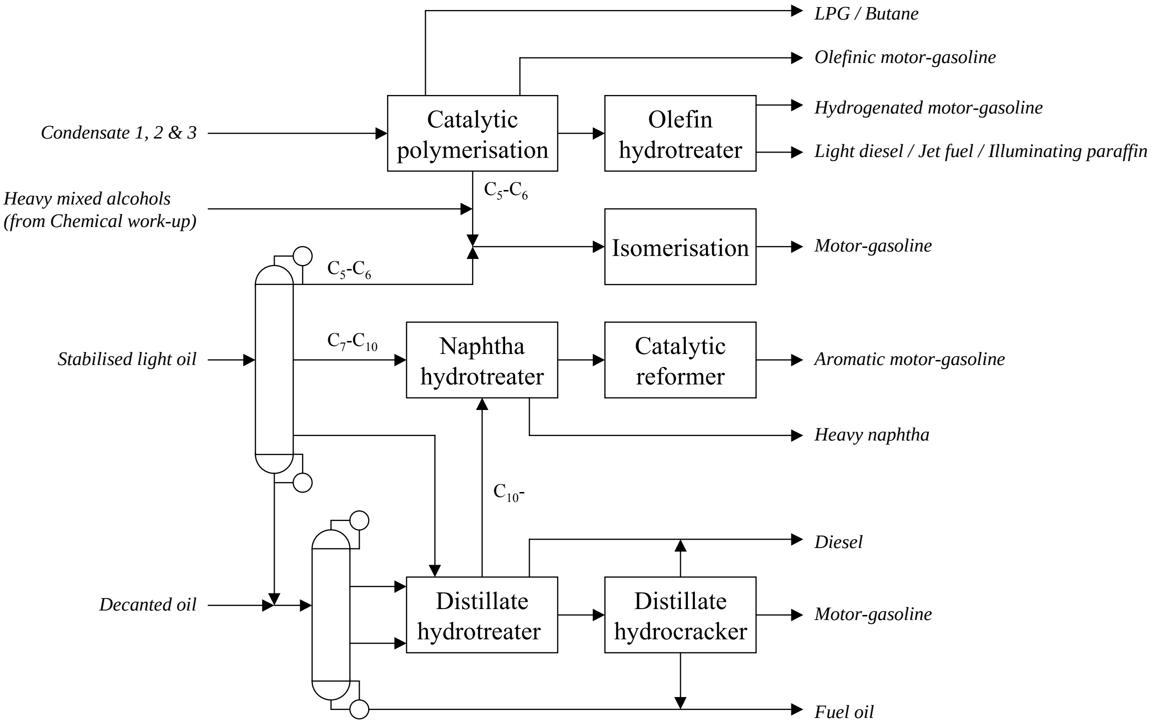

Figure 22. Block flow diagram of Sasol 2 and 3 condensate and oil work-up sections.

range products; b) Remove contaminants from Synthol oil to protect downstream catalysts and yield suitable products; c) Upgrade the quality of the motor-gasoline to meet octane specifications.

In order to meet the first of these objectives, the condensate work-up section employed solid phosphoric acid (SPA) catalysed olefin oligomerisation technology (CatPoly), which was known to work with Fischer-Tropsch products. Part of the product from this unit was hydrotreated. The second and third design objectives were met by designing the oil work-up section along similar lines as a second generation crude oil refinery, with an atmospheric distillation unit, naphtha hydrotreater (NHT), catalytic reformer (Platformer) and distillate hydrotreater (DHT). All of these units used standard crude oil technology. However, the overall refinery design was not second generation, but a third generation crude oil refinery design, with the inclusion of a vacuum distillation column and distillate selective cracker (DSC). The refinery design included only one typical Fischer-Tropsch refinery unit, namely an isomerisation unit to remove oxygenates and double bond isomerise the olefins.

It can retrospectively be argued that with more than two decades of HTFT refining experience Sasol might have known better than to adopt a crude oil refinery design. However, it should be realised that HTFT naphtha has a better octane number than crude oil(87) and that the crude oil refinery design adopted for Sasol 2 and 3 produced refined transportation fuels that met South African 1980 fuel specifications.

The UOP Catalytic Polymerisation technology was used for the olefin oligomerisation unit, which operated with solid phosphoric acid (SPA) catalyst. The olefin oligomerisation unit takes its feed from the Condensate 1, 2 and 3 streams, where it is fractionated in a feed debutaniser column, with the C_3-C_4 overheads fraction being used as feed for olefin oligomerisation and the C_5-C_6 bottoms fraction being sent to the isomerisation unit (Figure 23). The feed water content was adjusted by water injection to control the SPA catalyst hydration level.(88)(89)(90)(91) The oligomerisation unit consisted of two trains, each with four reactors having five catalyst beds with inter-bed quenches. The oligomerisation reaction is highly exothermic and part of the LPG fraction of the feed (propane and butane) is recycled to keep the temperature rise over the reactor within design parameters.

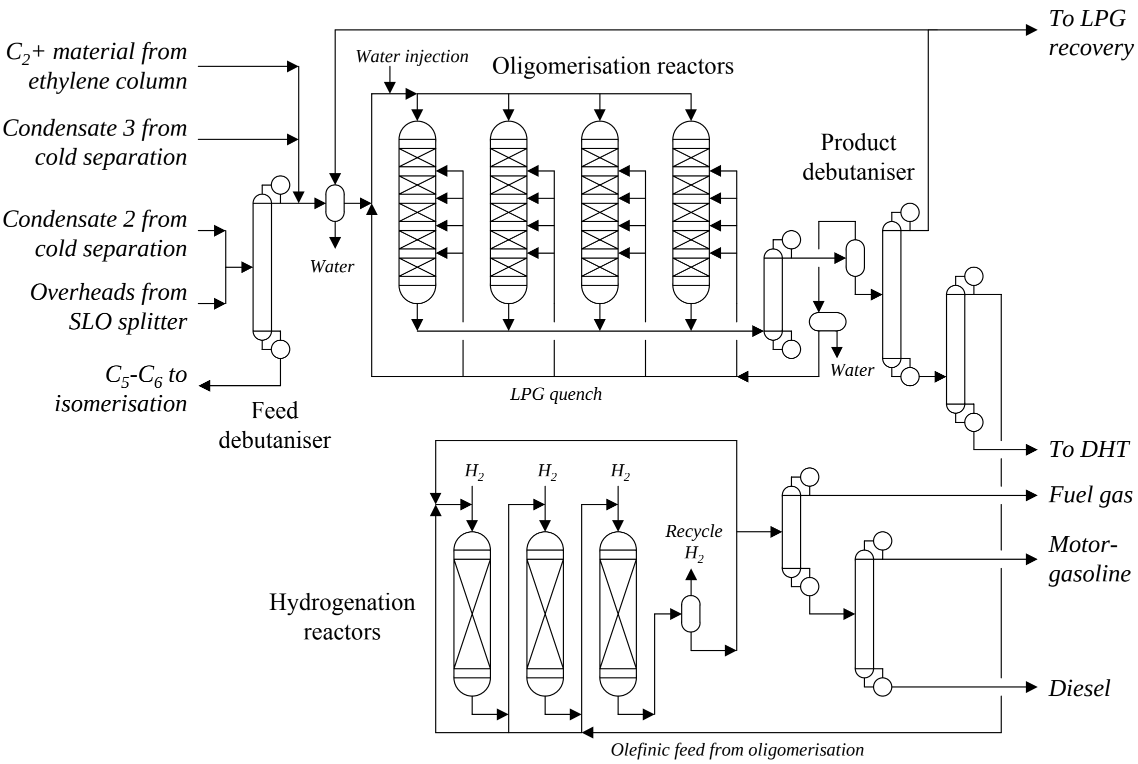

Figure 23. Catalytic polymerisation (CatPoly) process for olefin oligomerisation and the subsequent hydrogenation section (Polyhydrotreater) at Sasol 3. The CatPoly unit has two trains of four reactors each, but only train is shown.

At Sasol 2 the oligomerisation units were configured in such a way that it was possible to recycle part of the motor-gasoline fraction to boost overall distillate make. This was not done at Sasol 3 and the oligomerisation units therefore vary in design and operation. The unhydrogenated motor-gasoline has good octane (RON = 96.3 and MON = 82.3),(86) which is fairly insensitive to variations in feed composition.(92)(93)(94) The distillate range oligomers, as well as part of the motor-gasoline range olefins are hydrogenated. The octane number of the hydrogenated motor-gasoline was considerably lower(86) and varied over a wide range (RON =64-79 and MON=70-81).(95)

The olefin oligomer hydrogenation unit (Polyhydrotreater) consisted of 3 reactors, each loaded with a single bed of Co/Mo-Al_2O_3 catalyst and was operated in the range 260-350°C and 5 MPa, resulting in almost complete saturation of the olefins.

The C_5/C_6 isomerisation unit took its feed from the C_5/C_6 fraction from the Condensate streams and the SLO fractions. In addition to these feeds, some heavy alcohols (C_5+) from chemical work-up were sometimes co-processed. The isomerisation catalyst was a rare-earth exchanged Y-zeolite in a silica-alumina matrix[mm] and were used for double bond isomerisation and removal of the oxygenates in the feed. The reason for the selection of HZ-1 over more traditional alumina or bauxite catalysts is not clear. Alumina is a known dehydration catalyst and has later successfully been used in this unit with mixed Fischer-Tropsch feeds.(96) The unit consisted of two single bed reactors in parallel being operated in swing-mode at 370-410°C and close to atmospheric pressure. While the one reactor was converting C_5/C_6 material, the other reactor was being regenerated by controlled coke burn-off. A more detailed description of the reactions involved in this process is given elsewhere.(31)

The refining of the C_7+ fraction in the oil work-up section employed a conventional approach. A naphtha hydrotreater (NHT) was used to hydrogenate the feed for the catalytic reformer, mostly to remove oxygenates that would form water and cause corrosion problems. The reactor configuration was similar to that used for the hydrotreaters of the oligomerisation products shown in Figure 23. The same catalyst was initially used, but the operating conditions were more severe, with temperatures in the range of 320-420°C and an operating pressure of 6.0-6.5 MPa. The catalytic naphtha reformer was built using UOP Platforming™ technology and is of the continuous catalyst regeneration (CCR) type. This type of unit is well described in literature(97)(98) and the Sasol 2 and 3 units were designed for operation at 540°C and 1 MPa with a chlorided bimetallic Pt/Re-Al_2O_3 catalyst.[nn] Although a catalytic reformer is generally considered a source of high octane motor-gasoline, the low aromatic and naphthenic content of the Fischer-Tropsch feed resulted in a much lower conversion to aromatics than normally found (RON=87 at 84% C_5+ yield).(86)

The distillate hydrotreater (DHT) processed a mixture consisting of light vacuum gas oil (LVGO) and heavy vacuum gas oil (HVGO) from vacuum distillation, a side-cut from atmospheric distillation and the heavy product from the oligomerisation reactors. The DHT reactor contained four catalyst beds with inter-stage quenches and was operated in the range 290-380°C and 5.5-6.3 MPa. The product from the DHT was fractionated and the bottoms fraction served as feed to the distillate selective cracker (DSC).[oo] This was a much smaller unit, since HTFT technology produces little heavy material. The DSC used Mobil technology and the reactor contained a single bed of proprietary catalyst operated at 300-

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[mm] The catalyst employed was a cracking catalyst (see for example patent US 4,197,186). It is speculated that it may have been too active for this application.

[nn] Details of the catalyst composition and technology can be found in ref.(99).

[oo] The original Sasol 2 and 3 designs over-estimated the heavy-end fraction from HTFT synthesis and although two DSC reactors were built, only one was really needed.

415°C and 4.0-3.6 MPa. The product was fractionated to produce a poor quality motor-gasoline (RON<80), good diesel and small fuel oil fraction.

5.3.3. Sasol 2 and 3 chemical work-up

The sequence of primary separation at the Sasol 2 and 3 chemical work-up (Figure 24) is the same as that of Sasol 1 (Figure 17). The oxygenates in the reaction water are concentrated by the primary distillation column in the overheads fraction. The bottoms fraction consists of a dilute acidic solution and contains predominantly light carboxylic acids (1-2%). Most of the bottoms fraction is sent for biotreatment and some is used in the tail gas wash step after the Synthol reactors. The overheads fraction contains about 20% water and is further separated in the carbonyl stripper column to produce an overheads product that is rich in carbonyls (ketones and aldehydes) and a bottoms product that is rich in alcohols.

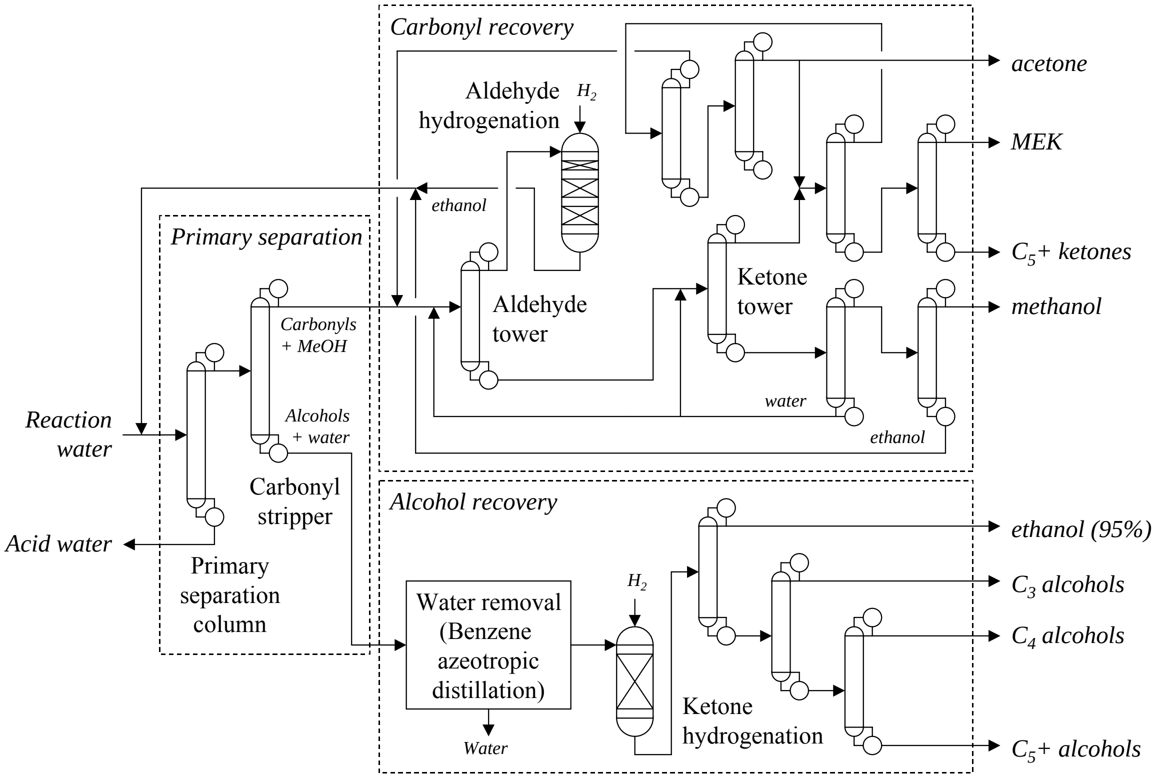

Figure 24. Chemical work-up section at Sasol 2, which is similar to that of Sasol 3.

The overhead product from the carbonyl stripper is sent to the carbonyl recovery section. The separation and processing sequence is similar to that of the Sasol 1 chemical work-up. The acetaldehyde is recovered in the aldehyde column and hydrogenated to produce more ethanol. In the ketone column the ketones are recovered overheads, while the bottoms product contained mainly water, methanol and some ethanol, which was further separated in subsequent columns. Unlike in the Sasol 1 design, the ketones were further purified to produce acetone and methyl ethyl ketone (MEK) as final products.

The bottom product of the carbonyl stripper was sent to the alcohol recovery section, which is similar to that used at Sasol 1. The water was removed by azeotropic distillation with benzene. This was followed by selective hydrogenation of the ketones in the alcohol mixture to produce alcohols. The alcohol mixture was then separated to produce ethanol, mixed propanols, mixed butanols and a heavier alcohol mixture. Not all of these steps were included in the Sasol 3 alcohol recovery section.

6. Mossgas gas-to-liquids technology (1980-1990's)

Despite the successes of Sasol 1, 2 and 3, South Africa's dependence on imported oil was still a point of concern for the South African government. In 1984 the Mossgas project was initiated to investigate the conversion of gas and associated natural gas liquids[pp] to transportation fuel.(100) The government gave the final go-ahead for the project in 1986 based on the Soekor gas find in the Bredasdorp Basin, off the coast of Mossel Bay.(101) The offshore platform landed its first gas in March 1992 and construction of the Mossgas facility was completed by the middle of 1992, achieving full production in January 1993.(100)(102)

The Mossgas facility was designed to produce 33 000 bpd products from the Fischer-Tropsch conversion of 200 000 $m^3 \cdot h^{-1}$ (normal) natural gas (22 500 bpd)[qq] and 70 $m^3 \cdot h^{-1}$ associated natural gas liquids (10 500 bpd). The project had capital cost of close to US$ 2.4 billion, but with the large unexpected drop in the oil price in the 1990's (less than US$ 20/bbl), the South African government was severely criticised for "wasting" tax payer's money. The project had a production cash cost of US$ 9-10/bbl, which nevertheless resulted in a significant operating profit.(100) The Mossgas gas-to-liquids facility is presently operated by PetroSA.

[pp] The natural gas liquids are also called gas condensates and should not be confused with HTFT Condensates.

[qq] The design figures quoted by PetroSA for the 3 Synthol reactors are 7 500 bpd, but in ref.(42) it is stated that the Mossgas Synthol reactors were designed for a production of 8 000 bpd. This increase in capacity is not due to the mechanical design, but is due to the synthesis gas composition. The synthesis gas contains less inert material resulting in higher H_2 and CO partial pressures, which causes the reactor productivity to increase.

6.1. Mossgas Fischer-Tropsch synthesis

The 1988 HTFT reactor design selected for the Mossgas project was the tried-and-tested commercial Sasol Synthol circulating fluidised bed (CFB) design, which was then in operation at Sasol 2 and 3.(20)

The Mossgas facility was operated with the same fused iron Fischer-Tropsch catalyst and Sasol Synthol operating conditions as the Sasol 2 and 3 facilities. The product distribution from HTFT synthesis was therefore similar to that reported for Sasol 2 and 3 (section 5.1), but the product slate of the feed to the refinery differed, due to the inclusion of natural gas liquids. The natural gas liquids are mainly aliphatic hydrocarbons, typical of a low sulphur paraffinic crude oil.

6.2. Mossgas gas loop

A process flow diagram of the Mossgas gas loop is shown in Figure 25.(102) The offshore production platform supplies the Mossgas facility with a mixture of natural gas (NG) and natural gas liquids (NGL). These feed materials are separated in the natural gas liquid recovery section. Part of the natural gas can also be liquefied in a liquefied natural gas (LNG) plant to provide a backup supply of gas (twenty-four hours) during upsets at the offshore production platform.(100) Typical compositions of the natural gas, natural gas liquids

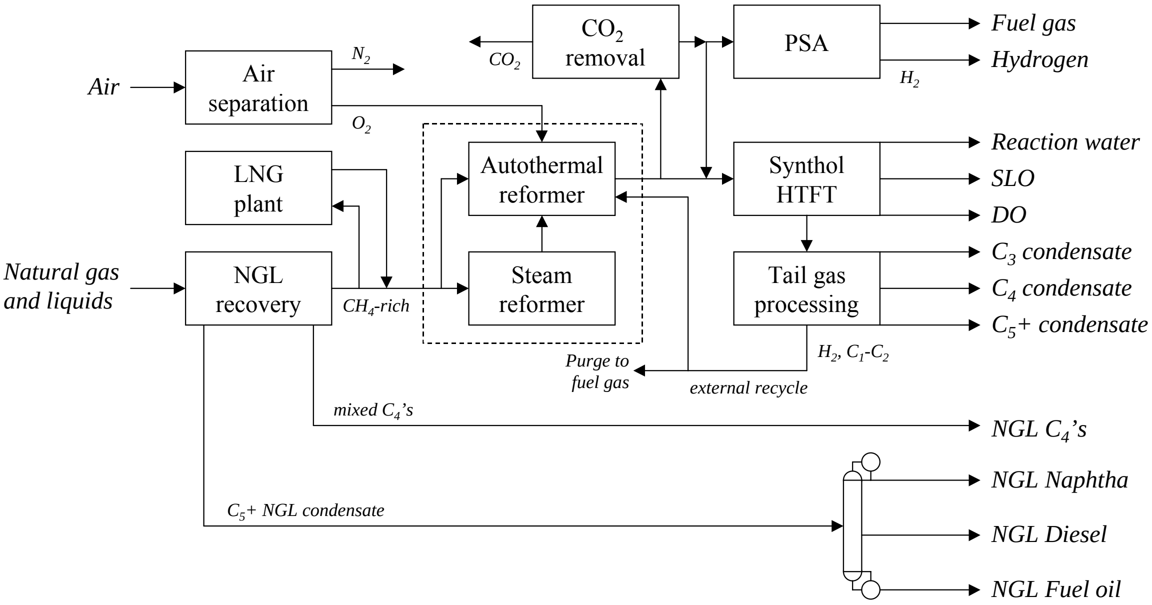

Figure 25. Mossgas gas loop.

and products from the NGL recovery section are given in Table 14. The condensate fraction from the NGL recovery section is further fractionated to produce a naphtha feed to the refinery, a straight run diesel blending component and a fuel oil fraction.

Table 14. Design composition of the natural gas (NG) and natural gas liquids (NGL) from the production platform, as well as the products from NGL recovery.

Compound	Feed material (mass %)		Products from NGL recovery (mass %)		
	NG	NGL	gas	C_4's	condensate
H_2S	8 ppm		8 ppm		
N_2	2.2	0.0	2.3		
CO_2	5.4	1.2	5.9		
H_2O	70 ppm	60 ppm	<0.1		
Methane	70.5	6.0	74.8		
Ethane	11.0	5.2	12.9		
Propane	6.4	8.7	3.9	0.5	
n-Butane	3.1	10.4	0.2	61.3	0.3
iso-Butane				37.1	0.0
Pentanes	1.4	68.5		1.1	16.8
Hexanes					7.1
C_7-120°C					21.2
120-180°C					21.1
180-400°C					29.2
>400°C					4.3

The methane-rich gas from NGL recovery is desulphurised and used as feed to gas reforming.(102) Mossgas employs the Lurgi Combined Reforming Process, which is a two step reforming approach. The primary reformer is a tubular steam reformer that is followed by a secondary autothermal reformer (ATR). Steam reforming[rr] is mainly used for hydrogen production, since it produces a H_2:CO ratio well above that required for Fischer-Tropsch synthesis. Part of the methane rich feed is bypassed and is combined with the product of the primary reformer, as well as the C_2 and lighter product from tail gas processing (external recycle) to serve as feed to the ATR. In the ATR the methane is partially combusted with

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[rr] The Mossgas steam reformer produces a H_2:CO ratio of around 7:1. Steam reforming is not considered the preferred technology for large GTL plants, since it has a poor economy of scale compared to ATR (ref.(80)).

oxygen from the air separation unit, steam reformed and subjected to the water-gas shift reaction over a nickel-based catalyst (Equations 6-8).(80) There are three identical reforming trains serving the three Synthol reactors and the synthesis gas to each Synthol reactor has a H_2:CO ratio of around 3:1.[ss,(100)]

Partial combustion: $2\ CH_4 + 3\ O_2 \rightarrow 2\ CO + 4\ H_2O$ ... (6)

Steam reforming: $CH_4 + H_2O \rightleftharpoons CO + 3\ H_2$ ... (7)

Water-gas shift: $CO + H_2O \rightleftharpoons CO_2 + H_2$ ... (8)

About 30% of the synthesis gas from the secondary reformer is sent to a Benfield unit for CO_2 removal. The remaining CO_2 in the synthesis gas is used to indirectly adjust the H_2:CO ratio in the Sasol Synthol reactor. This is possible because the fused Fe-based Fischer-Tropsch catalyst is active for the water-gas shift reaction. The synthesis gas composition is adjusted by the CO_2-free synthesis gas, which also serves as feed to the pressure swing absorption (PSA) unit for refinery hydrogen production.

The product from Sasol Synthol HTFT synthesis is cooled down in a similar way as shown in Figure 19 for Sasol 2 and 3. The products are decanted oil (DO),[tt] stabilised light oil (SLO), aqueous product (reaction water) and tail gas. Tail gas processing is much simpler than in the Sasol 2 and 3 gas loop, since the hydrogen, methane, ethane and ethylene are not recovered as separate products in a cold box, but recycled as a mixture to the ATR. Although this reduces the carbon efficiency of the Mossgas gas loop design, the capital cost associated with the gas loop is less. The heavier condensate products in the tail gas are separated by pressure distillation to yield C_3, C_4 and C_5+ condensate streams. Unlike the HTFT Condensate 1, 2 and 3 streams at Sasol 2 and 3, these condensates are proper distillation cuts, making refining more efficient.[uu]

[ss] This is a very high H_2:CO ratio, since HTFT Synthol requires a H_2:CO ratio of less than 2:1.

[tt] Decanted oil is strictly speaking the product from slurry oil after removal of the suspended catalyst particles in mixer-settlers to produce a gunk stream.

[uu] The C_3 condensate contains 87% propylene, 12% propane, 0.2% C_2 and 0.8% C_4 hydrocarbons; the C_4 condensate contains 85% butenes, 13% butanes and the remainder C_3 and C_5 hydrocarbons; the C_5+ condensate contains less than 1% C_4 material.

6.3. Mossgas refinery

The processing of natural gas liquids is integrated with the refining of the Fischer-Tropsch syncrude in the Mossgas facility. There is consequently not a separate work-up section dealing with natural gas liquids. The Fischer-Tropsch derived condensates are likewise integrated with the refining of the Fischer-Tropsch oil fraction. The refinery therefore consists of only two sections, namely an oil work-up to refine all the hydrocarbons and a chemical work-up to refine the water-soluble oxygenates in the reaction water.

6.3.1. Mossgas oil and condensate work-up

Although the Mossgas oil work-up section has been built scarcely a decade after Sasol 2 and 3, the design is clearly modelled on a fourth generation crude oil refinery (Figure 26).(102) The co-processing of natural gas liquids makes the design better suited to an oil refining approach, yet, the design also took far more cognisance of the nature of the Fischer-Tropsch products. For example, there is no vacuum distillation column and the refinery boasts an oligomerisation unit using the Conversion of Olefins to Distillates (COD) process that was specifically designed for the upgrading of Fischer-Tropsch olefins to diesel.

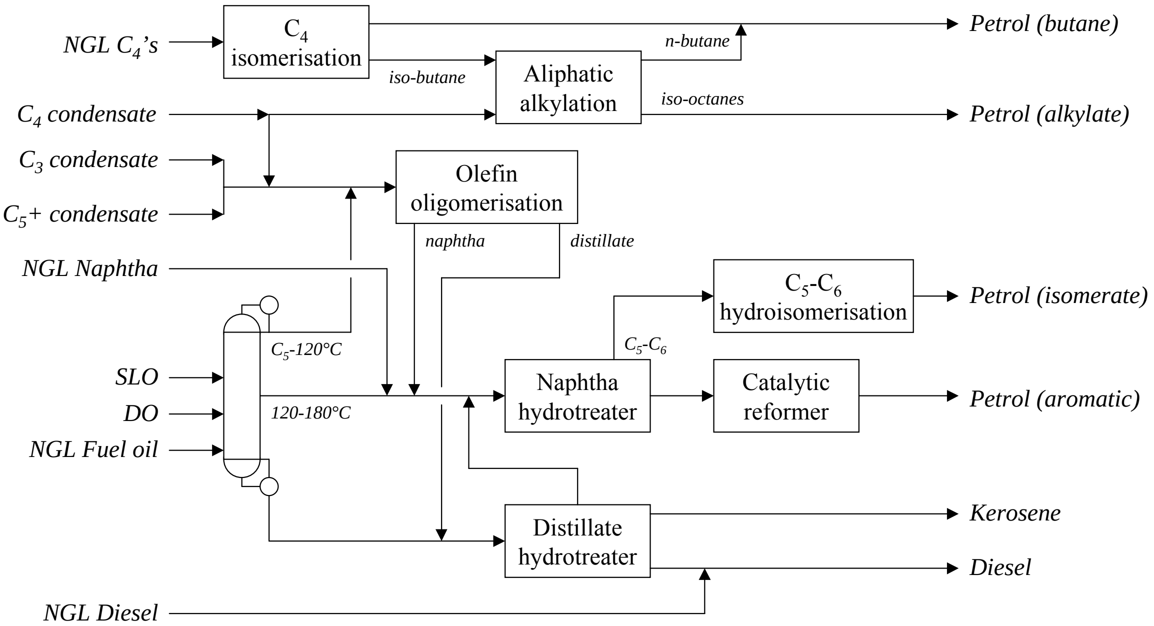

Figure 26. Mossgas oil work-up.

The abundance of butanes from the NGL recovery section and abundance of butenes from the HTFT condensate, make alkylate production a natural choice. The butanes are skeletally isomerised to produce iso-butane over a chlorided Pt-Al_2O_3 catalyst in an UOP Butamer™ process.(103) The iso-butane is then reacted with the HTFT derived butenes in a HF catalysed alkylation process from UOP to produce an alkylate rich in iso-octanes.[vv]

The HTFT C_3 condensate, HTFT C_5+ condensate and C_5-C_8 overheads fraction from SLO distillation are combined to provide an olefin rich feed to the COD process. This process has been developed in South Africa by the Central Energy Fund (CEF) and Süd-Chemie.(105) The process is in many respects similar to the Mobil Olefins to Gasoline and Distillate (MOGD) process(106) and also uses a ZSM-5 zeolite catalyst (Süd-Chemie COD-9).(107)(108) The mixture of olefins is converted in three reactors, which allows one of the reactors to be taken off-line for in situ catalyst regeneration by controlled carbon burn-off. For distillate mode operation, the operating conditions are typically 200-320°C and 5.5 MPa. The product consists of fuel gas, as well as propane, butane, COD gasoline and COD distillate.[ww] The distillate is of high quality (cetane 52-54), but of low density.(105)(109) The unhydrogenated COD gasoline is of a poor quality (RON=81-85, MON=74-75)(105) and is therefore reprocessed with the SLO naphtha. The fuel properties are inherent to the type of catalysis used.(110)

The C_9-C_{10} SLO fraction, NGL naphtha and COD naphtha form the combined feed to the naphtha hydrotreater (NHT). The NHT (UOP technology) is used as feed pretreatment for both the C_5-C_6 hydroisomerisation and catalytic reforming units to saturate the olefins and hydrodeoxygenate the oxygenates. The removal oxygenates are especially important, since both processes downstream from the NHT are sensitive to water. The hydroisomerisation unit uses UOP Penex™ technology(111) that is based on a chlorided Pt-Al_2O_3 catalyst, while the catalytic reformer unit uses UOP Platforming™ technology(98) that is also based on a chlorided catalyst. Both processes are used to produce final products.

The distillate hydrotreater (DHT) hydrogenates the COD distillate and the distillate from SLO distillation to produce diesel and kerosene. The straight run distillate from NGL recovery is combined with this product to make a final diesel fuel. The DHT is based on IFP

[vv] The selection of a HF catalysed process is somewhat surprising, since the HTFT product is rich in 1-butene, which is known to be the worst C_4 olefin feed for HF alkylation, resulting in a fairly low octane alkylate (RON=87-89). Conversely, using H_2SO_4 would have resulted in double bond isomerisation to produce a much better alkylate (RON=96-98). Ref (104), p.522.

[ww] Typical COD production figures are: fuel gas 1100 $m^3 \cdot h^{-1}$ (normal); propane 4 $m^3 \cdot h^{-1}$, butane 2 $m^3 \cdot h^{-1}$, COD gasoline 15 $m^3 \cdot h^{-1}$, and COD distillate 46 $m^3 \cdot h^{-1}$. Ref.(102)

(now Axens) technology.(100) Since the distillate is low in aromatics, it also finds a niche application as indoor heating fuel.

6.3.2. Mossgas chemical work-up

The chemical work-up section processes the reaction water of a similar composition to that of Sasol 2 and 3. Rather than separating the water soluble organic compounds, the carbonyls are partially hydrogenated to produce alcohols, thereby simplifying work-up considerably.(100) The carbonyl to alcohol hydrogenation is performed with a Süd-Chemie G-134 nickel on silica-alumina catalyst, which has proven to be very stable in this application and the refinery is still operating with part of its 1993 start-up batch of catalyst.(112) The anhydrous alcohol product produced after water removal can either be sold as solvent, or can be added to the diesel to produce a 5% oxygenated diesel.(109)

7. Shell gas-to-liquids technology (1980-1990's)

Shell started research into Fischer-Tropsch synthesis in 1973 and the work was originally focused on coal-to-liquids conversion. In 1980 the focus shifted to natural gas as a feedstock. The development of the Shell Middle Distillate Synthesis (SMDS) process began in 1983, when a pilot plant was constructed at the Shell Research and Technology Centre in Amsterdam.(113)

The first commercial gas-to-liquids facility to be built with the SMDS technology, was the 12 500 bpd plant in Bintulu, Sarawak, Malaysia. Discussions with the Malaysian government already commenced in 1985 and the Shell MDS (Malaysia) Sdn Bhd company was founded in 1986. The Central Luconia gas fields were identified as feed source. The process design package was completed in 1988. Construction started in November 1989, with mechanical completion being achieved early in 1993, followed by successful commissioning later in the same year.(114) After a plant turnaround, it was partly destroyed by an explosion in the air separation unit in December 1997. A new air separation unit was constructed and the plant was re-commissioned in May 2000. It has been in operation since then.(113)

7.1. Shell Bintulu Fischer-Tropsch synthesis

Due to the limitation that is imposed on the carbon number distribution from Fischer-Tropsch synthesis (Anderson-Schultz-Flory distribution) it is not possible to tailor-make a Fischer-Tropsch catalyst to produce products that are limited to a specific range. The approach adopted by Shell was to use the Fischer-Tropsch reaction to produce heavier products (high α-value), which could then be selectively cracked to the desired carbon number range.(115) For this purpose Shell developed a low temperature Fischer- Tropsch (LTFT) technology.

Catalyst selection was focussed not only on activity, but also on producing a catalyst with an α-value of 0.90 or higher.(114) The development of a new Fischer-Tropsch catalyst was also intrinsically linked to the selection of reactor-type to be used. Details of the reactor selection and fundamental work that was done in this regard has been published by Sie and co-workers.(114)(115) The main factor that resulted in the selection of a multi-tubular fixed bed reactor, was timing.[xx],(114) Other beneficial properties of multi-tubular fixed bed reactors that were cited were: high volumetric utilisation of reactor space by the Fischer-Tropsch catalyst, the ability to have a catalyst gradient along the reactor, no need for a solid-liquid separator and minimal catalyst attrition. The Fischer-Tropsch catalyst that was developed was based on cobalt,(116) not only due to the high α-value that could be obtained, but also because it was believed to be more stable than an equivalent Fe-based catalyst. The inability to replace catalyst during operation in a fixed bed reactor, as opposed to slurry bed and ebullating bed reactors, was therefore not a concern. The Shell Co-based Fischer-Tropsch catalyst could be regenerated in situ and had a useful catalyst lifetime of around 5 years.(116)(117)

The Shell Fischer-Tropsch synthesis process, called heavy paraffin synthesis (HPS), seems to have an α-value of around 0.91 based on its published product distribution.(117) Synthesis gas conversion of up to 95% with a C_5+ selectivity in the range 90-95% have been reported.(113) The Bintulu-plant has four multi-tubular reactors with a rated capacity of around 3000 bpd each. The catalyst is Co-based and Shell appears to have concentrated on the development of a silica support.(44) However, according to SRI(113) the catalyst is a promoted cobalt on a alumina based refractory oxide material, although it is more likely that the Fischer-Tropsch catalyst is based on zirconia.(118)

[xx] Scale-up of multi-tubular fixed bed reactors are comparatively simple, since each tube is essentially a reactor and piloting done on a single tube can be representative of commercial operation. The Sasol experience with Arge fixed bed reactors further proved that these reactors are stable and easy to operate. It had a low risk factor.

7.2. Shell Bintulu gas loop

The natural gas feed is converted into synthesis gas by partial oxidation with oxygen from an air separation unit (Figure 27). The partial oxidation unit uses the Shell Gasification Process (SGP) that was developed in the 1950's. The gasifiers are operated at 1300-1500°C and pressures up to 7 MPa, giving a carbon efficiency of 95% with a methane slip of 1%.(117) The SGP produces a synthesis gas with a H_2:CO ratio of 1.7:1, which is lower than the 2.15:1 usage ratio required for Fischer-Tropsch synthesis with Shell's Co-based LTFT catalyst.(113) The hydrogen deficiency is made up by a methane steam reformer, which operates at around 850°C and converts the methane to a hydrogen rich gas (H_2:CO>3) over a nickel catalyst.(117) Part of the synthesis gas production from the steam reformer is used to produce hydrogen for the refinery.

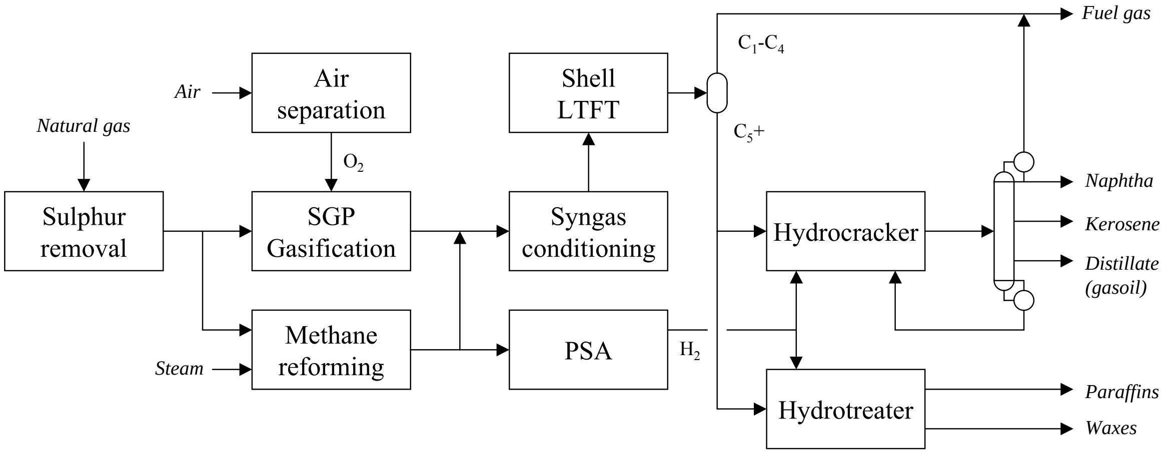

Figure 27. Process flow diagram of the Shell Bintulu facility.

After heat recovery, the cooled synthesis gas is cleaned by water scrubbing and passed over guard beds to remove potential Fischer-Tropsch catalyst poisons, such as sulphur compounds, before being used for synthesis.(116) Since high conversion is achieved during Fischer-Tropsch synthesis, the gas loop is not closed. The product from LTFT synthesis is stabilised and the C_1-C_4 fraction is used as fuel gas. The heavier hydrocarbons are used as feed material to the refinery

7.3. Shell Bintulu refinery

The refinery section employed to upgrade the products from LTFT synthesis is remarkably simple (Figure 27). It contains only two processing units, namely a hydrocracker and a hydrotreater.(119) The hydrocracker is operated in the range 300-350°C and 3-5 MPa with a proprietary hydrocracking catalyst from Shell (Pt or Pd on Al_2O_3).(113) The hydrocracker has four functions, namely, olefin hydrogenation, hydrodeoxygenation (HDO),[yy] hydrocracking and hydroisomerisation to produce preferably middle distillate.(115) The hydrotreater is employed for olefin hydrogenation and HDO to produce paraffins and wax for the chemicals market.

The product is fractionated and the unconverted wax-fraction can either be sold as a wax, or recycled to the hydrocracker. Depending on the hydrocracking severity, the product composition can be varied from 15% lights and naphtha, 25% kerosene and 60% gas oil in gas oil mode, to 25% lights and naphtha, 50% kerosene and 25% gas oil in kerosene mode. Some typical product properties are given in Table 15.(115)(116) Although the wax, paraffins and LPG can be sold as final products, the marketing of the fuels related products depend on Shell's ability to blend it with the products from their crude oil refineries to meet fuel specifications.

Table 15. Typical product properties from the Shell Bintulu LTFT refinery.

Property	Naphtha	Kerosene	Gas oil
Density @ 15°C ($kg{\cdot}m^{-3}$)	690	738	776
Boiling range (°C)	43-166	155-191	184-357
Aromatics (%)	0	<0.1	<0.05
Cetane index	-	58	76
Viscosity @ 40°C (cSt)	-	-	2.7
Smoke point (mm)	-	>50	-
Flash point (°C)	-	42	-
Freezing point (°C)	-	-47	-

8. Sasol gas-to-liquids technology (2000's)

In July 1997 a memorandum of understanding was signed between Sasol, Philips Petroleum and QPGC for the construction of a 20 000 bpd Fischer-Tropsch based gas-to-liquids plant in Ras Laffan, Qatar. Philips Petroleum withdrew after the collapse of oil prices in 1998. By mid-2001 a new agreement was reached, with Qatar Petroleum having a 51%

[yy] The product contains some primary alcohols, with other oxygenates being present in much lower quantities.

stake in the joint venture and Sasol a 49% stake. Natural gas from the Al Khaleej field was earmarked as feed for which the gas supply infrastructure was already developed by a joint venture between Qatar Petroleum and ExxonMobil.(120) This allowed front-end engineering and design of a 34 000 bpd facility to proceed, which was called Oryx GTL.(75)

The Oryx GTL plant achieved mechanical completion in 2006 and was officially opened in June 2006. The commissioning phase started in mid-2006 and the production of the first GTL products was announced in February 2007.(121) Commissioning problems are constraining output to 7000-10000 bpd and additional downstream equipment is required.(122)

8.1. Oryx GTL Fischer-Tropsch synthesis

The Oryx GTL plant uses LTFT technology based on the Sasol Slurry Phase Distillate™ process, using a newly developed Co-Al_2O_3 Fischer-Tropsch catalyst.(75)(123) The reactor technology has originally been developed and commercialised with an Fe-based LTFT catalyst at the Sasol 1 plant in the 1990's. A commercial 5 m diameter slurry phase reactor was commissioned in May 1993.(20) One of the main differences between the use of Co-based and Fe-based LTFT catalysts in the Sasol Slurry Phase Distillate™ process is catalyst lifetime, with the Co-based LTFT catalyst being more resistant to reoxidation by water, allowing it to be more productive under high per pass conversion operation.(48) Typical operating conditions are 230°C and 2.5 MPa.

The Oryx design uses two slurry bed reactors, each weighing 2100 ton and is about 60 m high and almost 10 m in diameter.(124)(125) The reactors were pre-fabricated and shipped due to the difficulty of on-site assembly.(75) The Co-based LTFT catalyst is manufactured by Sasol and Engelhard (now BASF) joint venture in a new catalyst preparation plant at De Meern, The Netherlands.

8.2. Oryx GTL gas loop

The gas loop design for Oryx (Figure 28) consists of autothermal reforming (ATR) of the natural gas, followed by LTFT synthesis and tail gas processing.(126) The natural gas feed is conditioned by removing sulphur over a ZnO guard bed and removing the coke precursors with a copper catalyst. The cleaned gas is preheated in the pre-reformer by heat exchange with the hot product gas from the ATR. The reformed gas is cooled to about 70°C to knock-out the water and ammonia in a water wash column, before it is used as feed to LTFT

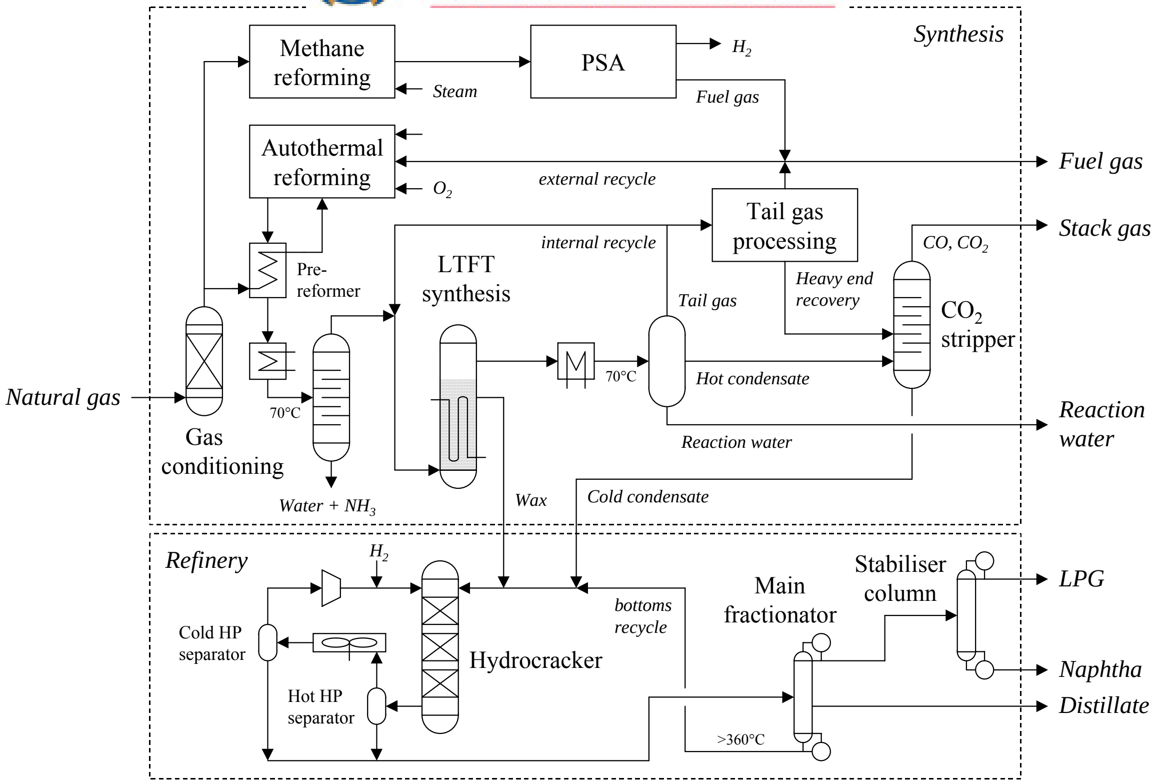

Figure 28. Process flow diagram of the Oryx GTL facility.

synthesis reactors. Part of the tail gas from LTFT synthesis is recycled to adjust the H_2:CO ratio from the ATR to the desired synthesis gas ratio for synthesis, called the internal recycle.

The product from LTFT synthesis is filtered in the reactor to separate the catalyst from the hydrocarbon product. The catalyst remains in the reactor and the hot wax goes through a secondary filtration step before being sent to the refinery. The wax-free gaseous products are cooled down to about 70°C to condense hydrocarbons and water. The hydrocarbon fraction (hot condensate) is phase separated from the aqueous product (reaction water) that contains some dissolved oxygenates, like methanol. The gaseous product is called the tail gas. The tail gas that is not used for the internal recycle, is cryogenically cooled to condense the C_3+ hydrocarbons and some water, which is called the heavy end recovery stream. The heavy end recovery stream and hot condensate are passed through a CO_2 stripper column, where the dissolved CO and CO_2 are separated, before it is sent to the refinery as a cold condensate. The uncondensed gas contains mainly C_1-C_2 hydrocarbons, H_2, CO and CO_2. Part of this product is recycled directly to the ATR as an external recycle, with the rest being purged for use as fuel gas.

A separate steam reformer is used to convert some of the natural gas into a hydrogen-rich synthesis gas. The hydrogen is recovered in a pressure swing absorption (PSA) unit for use in the refinery, while the hydrogen lean product is sent to the fuel gas system.

8.3. Oryx GTL refinery

The basic refinery design (Figure 28) is very similar to that used for the Shell Bintulu refinery that was shown in Figure 27. The refinery section receives two feed streams, namely wax and condensate that are combined to serve as feed to the hydrocracker. The hydrocracker is the only conversion unit in the refinery and uses ChevronTexaco Isocracking™ technology with a Chevron hydrocracking catalyst. The hydrocracking catalyst is a commercially available sulphided base metal catalyst on an acidic support. Typical operating conditions are a LHSV of 1.2 h^{-1}, 350°C and 7 MPa, with the temperature being adjusted to keep the per pass conversion at around 65%. The product from hydrocracking is distilled to produce LPG (3-7%), naphtha (20-30%) and distillate (65-75%), with the unconverted >360°C waxy product being recycled to the hydrocracker.(127)

The reaction water is separated by distillation into an alcohol-rich overheads product that is incinerated and a carboxylic acid containing water product that is biologically degraded to purify the water. No oxygenates are recovered from the reaction water.

Table 16. Typical properties of the products from a Co-based Sasol Slurry Phase Distillate™ process in combination with a hydrocracker as it is used in the Oryx GTL refinery.

Property	Naphtha	Distillate
Density @ 15°C (kg·m^{-3})	685-687	769-777
Boiling range (°C)	51-131	151-334
Aromatics (%)	0.3	0.5
Cetane number	39	72
Viscosity @ 40°C (cSt)	-	2.0-2.4
Flash point (°C)	-20	58
Freezing point (°C)	-	-15
Lubricity, HFRR (mm)	-	617
Net heating value (MJ/kg)	-	43.79

The products from the Oryx GTL refinery (Table 16)(127)(128)(129) are similar to those from the Shell Middle Distillate Synthesis process, since they use a similar refining methodology to process similar syncrudes. The naphtha has a low octane value (RON=50-55) with a *n*-paraffin:iso-paraffin ratio of 60:40.(127) The degree of branching is determined by the hydrocracker operation. The naphtha makes a good steam cracking feedstock(128) and the intention is to market it as such. The distillate has virtually no sulphur and has a high cetane number, but lacks the density to meet international diesel fuel specifications. The intention is to sell it as a diesel fuel blending stock. The simple refinery design used for Oryx GTL consequently suffers from one major drawback, namely that it does not produce transportation fuels or chemicals, only intermediate products and LPG. To upgrade the Oryx GTL product slate to final products, a more complex refinery is required.

9. Evolution of Sasol Fischer-Tropsch refineries

Over the past 30 years significant changes occurred in fuel specifications, which included the phasing out of leaded motor-gasoline, sulphur reduction and more stringent octane number and cetane number specifications. These changes, often motivated by environmental concerns, affected refineries by requiring changes in their product specifications and the emission standards of their refining processes. It affected refineries world-wide and necessitated modifications and changes to remain viable. There were also changes imposed by catalyst manufacturers, who developed new catalysts and phased out older catalyst types, as was the case with equipment. Unless refineries were designed with foresight, as some were, this forced refiners to continuously play catch-up. In the context of Fischer-Tropsch refining it was no different. The South African Sasol 1 refinery is more than 50 years old and sections of the original plant are still in operation. Although fuels are no longer produced at Sasol 1, it had to endure some changes with respect to fuels and chemicals production. Recently Sasol 2 and 3, which are more 20 years old, required a large capital investment in order to meet new fuel specifications.(130) The other commercial Fischer-Tropsch refineries, Mossgas, Shell Bintulu and Oryx GTL, are all comparatively new and have not yet needed changes to remain viable.[zz]

Fuel specifications and environmental legislation are not the only change drivers. There are ample opportunities to use Fischer-Tropsch synthesis as a platform for petrochemicals. Many chemicals that must otherwise be specifically synthesised, are produced in significant quantities during Fischer-Tropsch synthesis, like linear α-olefins, carboxylic acids, alcohols, ketones and waxes. The recovery of these chemicals affect fuel production and in itself caused Fischer-Tropsch refineries to evolve.

[zz] Neither the Shell Bintulu plant, nor the Oryx GTL plant is aimed at on-specification final fuels production.

9.1. Evolution of Sasol 1

The Sasol 1 plant was designed to produce fuel, yet, the main change driver had been the extraction of chemicals, rather than complying with new fuel specifications. The process to recover and produce chemicals started in 1958 with the production of ammonium sulphate (Figure 14) from the ammonia recovered in the Phenosolvan process. In the 1990's, when the LTFT slurry bed reactor was commissioned and the old Kellogg CFB reactors were decommissioned, Sasol 1 became a chemicals-only production facility.

Many of the major changes took place in the 1960's after a decision in 1962 to expand production in the direction of chemicals. The nitrogen from the air separation plant was converted into ammonia, in an ammonia synthesis plant commissioned in 1963.(35) Butadiene and styrene were produced and sold for synthetic rubber manufacturing. In 1964 Gaskor was founded to supply local industries with methane-rich gas and a pipeline to the Iscor steel works in Vanderbijlpark was completed in 1966.(35) In 1966 the first naphtha cracker was built to produce ethylene for Safripol (Suid-Afrikaanse Poli-olefiene, Engl. Transl. "South African Polyolefins") and was followed by a second cracker in 1969 to keep up with ethylene demand for the production of high density polyethylene (HDPE).(75) With all the chemicals extraction and production units, the product diversity from the Sasol 1 became impressive. It included: Motor-gasoline, diesel, kerosene, fuel oils, LPG, bitumen, sulphur, fuel gas, ethylene, propylene, butadiene, styrene, liquid nitrogen, liquid oxygen, argon, carbon dioxide, paraffin waxes, oxidised waxes, C_2-C_5 alcohols, acetone, methyl ethyl ketone (MEK), creosote, tar acids (phenols, cresols, xylenols), aromatic solvents, aliphatic solvents and ammonia derivatives.(35)

The construction of the inland oil refinery Natref next to Sasol 1 created new fuels opportunities and on 5 July 1971 a new formulation of petrol was marketed. The combination of crude oil and syncrude derived fuel proved to be remarkably beneficial.

The design requirements for refineries in the 1950's did not place the same emphasis on emissions and environmental impact as is current design practice. Early in the 1970's changes were made to address this shortcoming in the Sasol 1 design. Electrostatic precipitators were added to the power stations and these were commissioned in October 1972. The rotten egg smell caused by hydrogen sulphide emissions from Rectisol was addressed by routing the gas to a Stretford process for sulphur removal. However, the gas composition and material of construction proved incompatible and this unit was never successfully commissioned.(75) The Sasol Clean Air Technology (SCAT)(131) was developed to address this problem, but this technology was never commercialised. Inhabitants of Sasolburg had to wait until 2005 for this problem to be solved, when in 2004 Sasol 1 was converted from a coal-to-liquids facility into a gas-to-liquids facility by importing gas from Mozambique.[aaa],(132)

During the commissioning of Sasol 2 and 3, a pipeline was also constructed between Secunda and Sasolburg. With the large quantity of ethylene that became available, it was no longer economically viable to keep the two naphtha crackers at Sasolburg operational and these were decommissioned in 1983. However, demand for ethylene kept increasing and in 1988 one of the naphtha crackers was re-commissioned as an ethane cracker, to convert ethane from the Secunda plants into ethylene.(75)

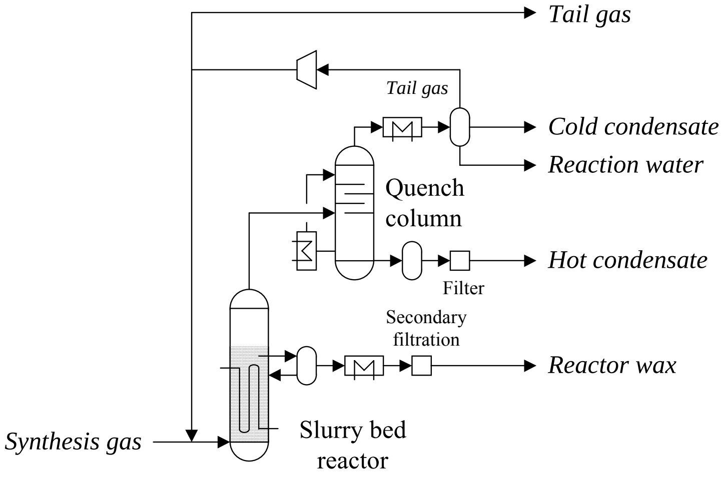

Figure 29. Sasol 1 slurry bed reactor flow diagram.

Due to its much smaller size, Sasol 1 became the test bed for new reactor technologies, with a 1 m diameter demonstration unit to test the Sasol Advanced Synthol (SAS) fixed fluidised bed in the 1980's and the Sasol Slurry Bed Process (SSBP) in 1990.(20) The success of these two projects led to significant changes at all Sasol's operations. A commercial scale diameter slurry bed reactor (Figure 29)[bbb] was commissioned at Sasol 1 in 1993,(20)(48) which paved the way for converting Sasol 1 to a chemicals-only facility. The product slate could be simplified by having only LTFT synthesis and the Sasol 1 process

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[aaa] A pipeline was constructed to import gas from Mozambique and the gasification section at Sasol 1 was modified with the addition of autothermal reformers (ATR). The Lurgi gasifiers were kept in operation along side the ATR's for some time.

[bbb] The 5 m diameter slurry bed reactor was designed for a synthesis gas capacity of 182 000 $m^3 \cdot h^{-1}$ (normal) with on-line removal and addition of catalyst. It uses a similar precipitated Fe-based Fischer-Tropsch catalyst as the Arge LTFT reactors and typical operating conditions are 245°C and 2.1 MPa.

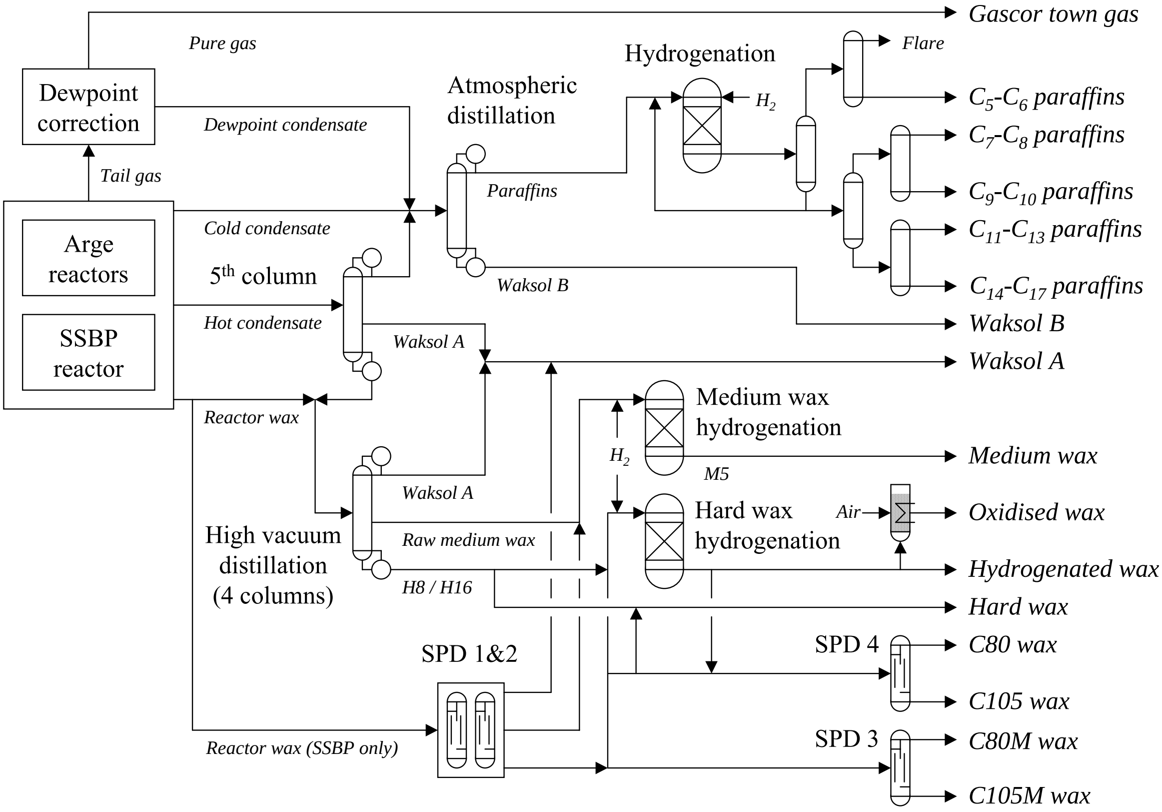

Figure 30. Sasol 1 refinery flow diagram in the mid-1990's.

configuration after the addition of the SSBP (Figure 30) is significantly different to that of the original design (discussed in Section 4).

The atmospheric distillation unit (ADU) separates the lighter fractions into paraffins and Waksol B. The feed materials to the ADU are caustic washed cold condensate (not shown in Figure 30; see Figure 16 for details), dewpoint condensate and the overheads from the 5th column. The paraffins are separated in different cuts that are sold to the solvent market, while Waksol B is sold to the fuel market. The 5th column, so called because it is the fifth column that forms part of the high vacuum distillation section, has a bottom temperature of 215°C and is operated at 14 kPa absolute pressure to avoid wax cracking. The Waksol A (or gatsch) overheads product is a waxy oil that is sold to the fuel market, while the bottoms product is combined with the reactor wax to serve as feed to the four columns in the high vacuum distillation (HVD) section (Figure 16). The medium wax that is recovered as an overheads product from the second and third columns have a congealing point of 51°C and is combined with the overheads product from the fourth column that has a congealing point of 62°C. This combined medium wax product is hydrogenated (Ni-based catalyst, 160°C and 2-3 MPa) and sold to the market, typically for use in candle manufacturing. The bottoms product is hard wax, which has a slightly brown colour. The wax is hydrogenated in two reactors in series (Ni-based catalyst, 230°C and 4.5-5.5 MPa) in flooded up-flow mode, with hydrogen being added only to the first reactor. Details of the wax hydrogenation process and the catalysis involved can be found elsewhere.(64) Part of the hydrogenated hard wax production is converted into various grades of oxidised waxes by partial air oxidation in batch reactors. The chemistry and principle of operation has been discussed elsewhere.(133)(134)

When the slurry bed reactor was installed, the wax distillation capacity became insufficient. A new section making use of short path distillation (SPD) was constructed. The method of distillation is therefore very different and allows the production of hard wax cuts with congealing points of 80°C (C80 and C80M waxes) and 105°C (C105 and C105M waxes) respectively. These columns were subsequently replaced by an even more efficient distillation configuration.

The evolutionary process is still on going, with imported material from the Secunda facility enabling the continued operation of phenolic extraction,[ccc] which was recently expanded with the commissioning of a Tar Naphtha Phenol Extraction (TPNE) plant.(135) The chemical work-up section is also kept operational with material imported from Secunda. Other chemicals production facilities that were added to the Sasol 1 portfolio included plants such as the synthesis of methyl iso-butyl ketone (MIBK) and methyl iso-butyl alcohol (MIBC) from acetone over a Pd on acidic resin catalyst (Amberlyst CH28).(136)

9.2. Evolution of Sasol 2 and 3

Sasol 2 and 3 are no longer known by these names. The two refineries became so integrated that they are now called Sasol West and Sasol East and the refinery complex is collectively known as Sasol Synfuels. Unlike Sasol 1, it remained a coal-to-liquids facility and it also remained an HTFT facility.[ddd]

In June 1995 an 8 m diameter Sasol Advanced Synthol (SAS) fixed fluidised bed reactor was commissioned at Secunda. The SAS technology proved to be more efficient than the Synthol CFB technology, although both use the same fused iron catalyst and produced a similar product slate.(42) The success of the first SAS led to the decision in March 1996 to

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[ccc] With the conversion of Sasol 1 from a CTL facility to a GTL facility, the tar products obtained by low temperature gasification in Lurgi gasifiers were no longer produced at Sasol 1. This would have implied closure of the tar processing facilities at Sasol 1, but it was decided to import material from Secunda and keep these facilities operational.

[ddd] Capacity growth on natural gas that will be imported from Mozambique is currently being planned.

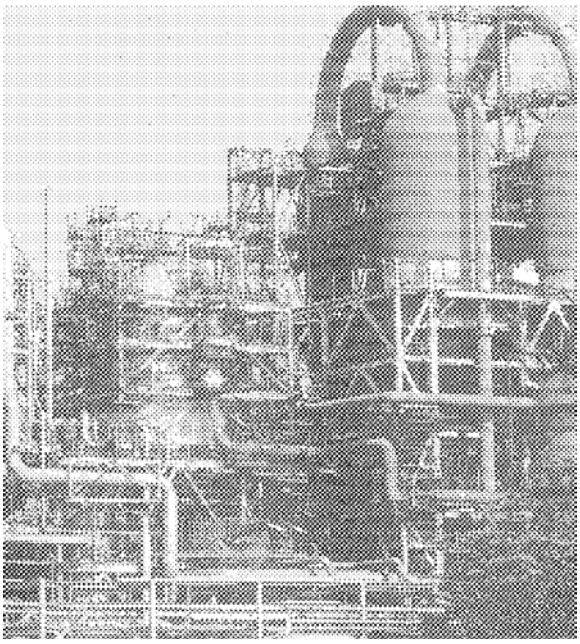

Figure 31. The construction of new SAS reactors next to the Synthol CFB reactors at Sasol Synfuels in Secunda. One SAS reactor replaces approximately two Sasol Synthol CFB reactors, yet it is much smaller in size. (This figure has been reproduced directly from Ref.(75) and is copyright protected).

change the Fischer-Tropsch synthesis section and replace all the old gooseneck Synthol CFB reactors that were so typical of Sasol, with SAS reactors (Figure 31). The synthesis sections at Sasol West and East each have two trains of 4 Synthol CFB reactors and it was decided to install one 8 m diameter and one 10.7 m diameter SAS reactor per train.[eee] The first new SAS reactor came on stream in September 1998 and the last SAS reactor in February 1999. A ninth SAS reactor (8 m diameter) was added in 2001 to serve as backup.(75)

The commissioning of the 120 000 tpa polypropylene plant at Secunda during late 1989, early 1990, heralded the start of new chemicals production era.[fff,(75)] The polypropylene plant was built using BASF technology and Secunda Synfuels refineries were affected only by the addition of a propylene-propane splitter and extraction of some propylene. There were also risk-mitigation projects associated with polymer production, like the Dimersol™ E plant(137) that converted ethylene to motor-gasoline during upset conditions.[ggg] Further extraction of propylene would follow in later years to feed chemical

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[eee] With Secunda synthesis gas and operating conditions the 8 m diameter SAS has a capacity of around 11 000 bpd and the 10.7 m SAS has a capacity of around 20 000 bpd.

[fff] The original plant had cost R 540 million and during the 1990's a further R 280 million was spent, increasing the output from the plant to 220 000 tpa. Ref.(75)

[ggg] The plant was built with IFP technology and used a homogeneous Ni-based catalyst to produce mainly C_4 and C_6 olefins from ethylene. It was expensive to keep the plant idling and alternative uses for the plant had

projects like the production of acrylic acid and 1-butanol.[hhh] The second major expansion in the polymer field came in 2006, with the addition of new polyethylene and polypropylene facilities as part of project Turbo.(130)

Probably the best-known expansion drive of Sasol in chemical production was the various α-olefins purification processes. Linear α-olefins in the C_4-C_8 range are used as co-monomers for the production of polyethylene.(138) The price is mainly determined by the cost of ethylene, which gave Sasol a significant cost advantage, since Sasol could recover these molecules by extraction from the HTFT product.(139) The extraction process to recover 1-hexene requires an etherification step to remove the close-boiling olefins and is similar to that used for the purification of 1-butene from cracker raffinate.(140) In 1992 a pilot plant was constructed for the purification of 1-pentene and 1-hexene, which was followed by a twin-train plant at Secunda to produce 100 000 tpa 1-pentene and/or 1-hexene. After debottlenecking the capacity was increased to 140 000 tpa and in 2000 a third 1-hexene train was added with a capacity of 80 000 tpa. This gave Sasol about 25% of the global market share for 1-hexene.(75) The marketing of 1-pentene was not successful despite the benefits of using it as a co-monomer,(141)(142) since Sasol would globally be the sole-supplier. The extraction of 1-octene followed in 1999, with the construction of a 50 000 tpa extraction plant. The purification of 1-octene required a different process configuration and it is significantly different to that employed for 1-hexene purification. It uses extractive distillation to remove the oxygenates and super-fractionation to purify the final product. In the first 1-octene train the carboxylic acids were neutralised with potassium carbonate before oxygenate extraction with NMP, but in the second 1-octene train the neutralisation step could be eliminated by applying azeotropic distillation for acid removal.(143) Due to the increasing demand for 1-octene, a third train has been approved, which has to use a synthetic route for the production of 1-octene from 1-heptene, since the first two trains have recovered all the 1-octene in the syncrude.[iii],(144)

The technology to purify linear α-olefins for the co-monomer market was also applied to the C_{12}-C_{13} range material. These detergent range olefins were purified and then hydroformylated with CO and H_2 over a classic Rh-based catalyst(145) in an OXO-process

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been actively sought in the late 1990's. It was eventually decommissioned and the capital written off, although some of the equipment are still in theory available for re-use.

[hhh] Although the acrylic acid and 1-butanol plants are using propylene from the Secunda facility, these plants were constructed at the Midlands site in Sasolburg (across the road from Sasol 1).

[iii] The capital cost of this 100 ktpa facility is estimated at R 2.1b and should be ready for operation in 2008.

licensed from Davy Process Technology.[iii] The aldehydes thus produced are hydrogenated to alcohols for the detergent alcohol market.(146) The Safol detergent alcohols (DA) plant was commissioned in 2002.

The Secunda facility was also expanded to produce chemicals in support of Sasol Solvents business unit. In June 1996 the *n*-propanol purification plant was commissioned, with a capacity of 45 000 tpa, which is 30% of the world production. In September 1999 a high purity (99.99%) ethanol plant was commissioned.(75) Both plants separated and purified molecules present in the HTFT syncrude. Kvaerner technology was used for a process to convert ethanol into ethyl acetate(147) and this plant was commissioned in May 2001.

A delayed coker plant was added to the tar value chain in the late 1990's, mostly with the aim of producing anode coke. The design is very flexible and allowed the production of various types and grades of coke, although it is not suited for the production of anode coke, due to thermal expansion coefficient of the coke. This unit affected the tar refinery (Figure 21) by producing typical by-product streams like coker naphtha that had to be processed in the CTN hydrogenation units and coker gas oil that had to be processed in the creosote hydrotreater.

Other chemical production facilities were also constructed, but these have since been decommissioned. Acetaldehyde was used to produce crotonaldehyde by successive aldol condensation and dehydration steps. The crotonaldehyde could then be hydrogenated to produce 1-butanol. The aldol condensation step was difficult to control, causing a lot of off-specification product to be produced. This plant was eventually shut down and a 1-butanol plant based on propylene hydroformylation was built. Presently the acetaldehyde is hydrogenated to produce ethanol, using the same approach as in the original Sasol 1 design (Figure 17). An acid recovery pilot plant was built in the chemical work-up section to recover acetic acid and propionic acid from the bottoms product of the primary separation column (Figure 24). This stream contains about 1-2% carboxylic acids and is quite corrosive. It was found that the carboxylic acids could be selectively extracted with methyl tertiary butyl ether (MTBE). However, corrosion problems and equipment failures, resulting in poor on-stream time, plagued the pilot plant at Secunda. Furthermore, to scale-up this process to commercial scale would have required a large MTBE inventory, as well as the largest diameter extractor in the world, which made it a very energy intensive process.(75) Acid recovery was therefore never taken beyond the pilot plant stage.

[iii] Originally Kvaerner, then became Davy Process Technology that was recently bought by Johnson Matthey.

Irrespective of all the chemical production projects, Sasol Synfuels at Secunda is still mainly a fuels refinery, with some chemicals co-production.[kkk] It benefited from the pre-2000 South African fuel specifications, which allowed a motor-gasoline rich in olefins and short on octane before lead addition. The olefin content in the final fuel was limited to 30% only by an internal Sasol specification. Furthermore, the oil work-up section had been designed along similar lines as a second generation crude oil refinery with only some third generation units included in the design (section 5.3.2). The refinery was therefore poorly designed to cope with the changes in international fuel specifications that were being debated in the 1990's, for example Euro-3 and Euro-4, especially with respect to the olefin content of motor-gasoline. Yet, the only refinery unit for octane production that was added before 2000 was a catalytic distillation column for the production of tertiary amyl methyl ester (TAME)^(148)^ and since then only a pentene skeletal isomerisation unit (IFP technology)^(149)^ was added to increase TAME production (Figure 32).

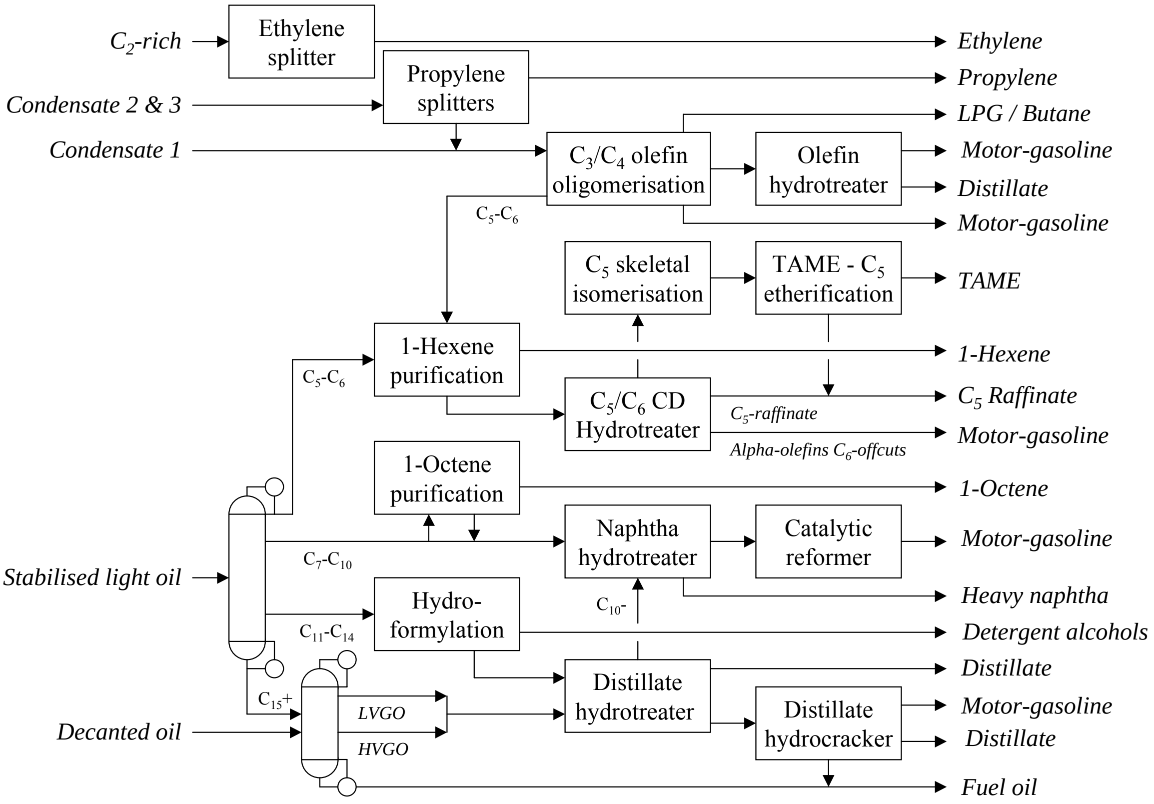

Figure 32. Sasol Synfuels oil and condensate refinery in 2004, before the refinery changes that were implemented with the construction of additional units for project Turbo.

[kkk] Fuels production at the Sasol Synfuels refineries year on year contribute more than 50% to the overall profit of the Sasol group of companies, making it the single most important asset and cash cow for growth. The operating profit of Synfuels for the second half of 2006 was R 8 360m, 69% of the operating profit of Sasol.

The first major change in South African fuel specifications came with the phase-out of leaded motor-gasoline. The impact of this on Sasol Synfuels was limited, since it coincided with the introduction of "Dual fuel™" that used methylcyclopentadienyl manganese tricarbonyl (MMT) as lead replacement. This was only an interim measure, since the South African fuel specifications that were legislated in June 2006 required no intentional metal addition to motor-gasoline, although provision was made for lead replacement petrol (LRP).[lll] The phasing out of LRP is expected.

The trend was nevertheless clear and the intention of lowering the benzene content to 3% in 2008 and 1% in 2012 has been announced.[mmm] A limitation on the olefin content of motor-gasoline may possibly be on the cards, as well as various other changes to bring South African specifications in line with European specifications. This threat has been identified by Sasol and resulted in project Turbo (Figure 33), a proactive attempt to ready Sasol Synfuels for the anticipated changes in fuel specifications.(130) Project Turbo is a R 13 billion project,

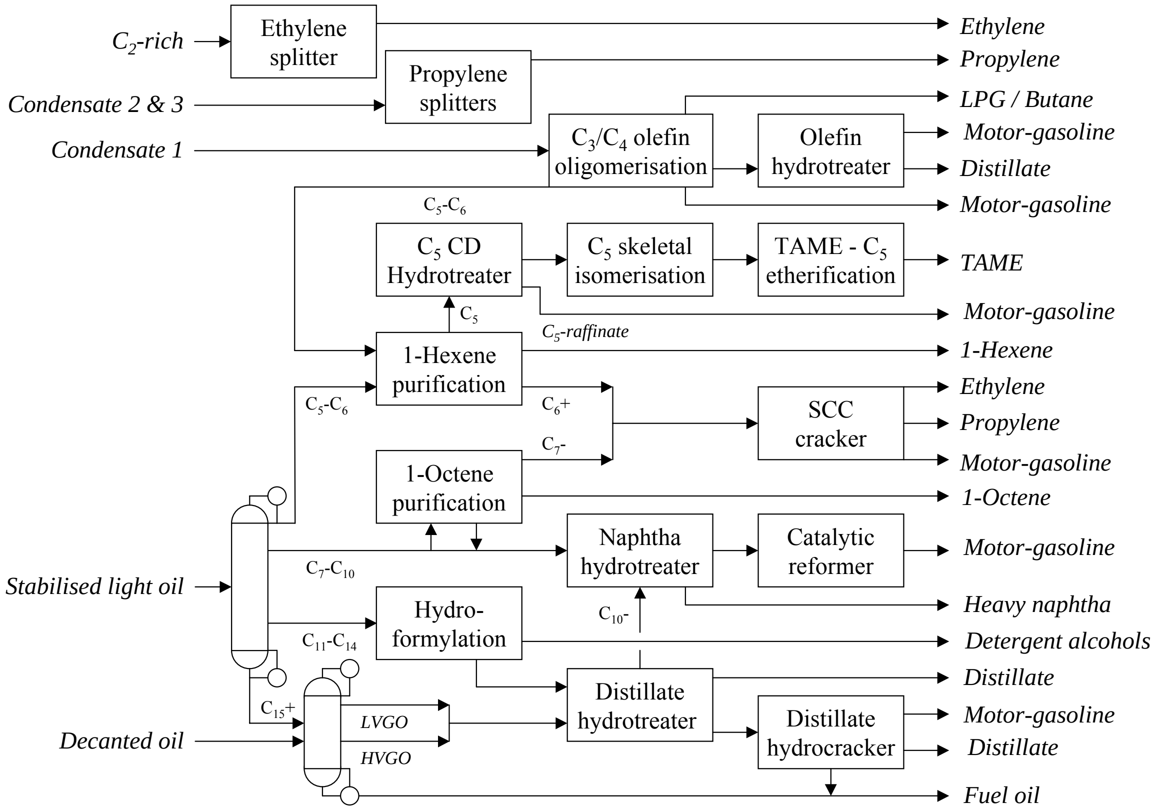

Figure 33. Sasol Synfuels oil and condensate refinery in 2006, after construction of project Turbo to meet the anticipated future South African fuel specifications.

[lll] Legislation published by the Department of Mineral and Energy affairs (DME) in the government gazette Vol.492 no.28958 on 23 June 2006.

[mmm] This timetable has since been moved out, with 3% benzene in fuel being required much later.

of which 40% of the cost is associated with upgrading the refinery, while the rest of the cost is associated with an expansion of the polymer business linked to the Synfuels refinery.[nnn] As interim measure, other less costly changes were implemented to increase the fuel quality.(150)

The construction of a high temperature fluid catalytic cracker as main refinery intervention to meet future fuel specification, was more aimed at chemicals production rather than fuels. The KBR Superflex™ Selective Cracking (SCC) technology,(151)(152) has been selected for this purpose. The refining philosophy underlying this decision is to convert the lowest quality fuel components into chemicals, namely ethylene and propylene, rather than upgrading the quality of the fuel per se. According to the SCC design, a high-octane aromatic motor-gasoline will be co-produced.[ooo]

Other changes are also being implemented, such as the separation of the olefinic feed to the oligomerisation units into a butene-rich feed to Sasol East and a propylene-rich feed to Sasol West. This would increase the octane number of the hydrogenated motor-gasoline at Sasol East(33) and increase the distillate production at Sasol West.(154)

10. Future Fischer-Tropsch refineries

10.1. Change drivers in Fischer-Tropsch refining

When considering Fischer-Tropsch refineries of the future, the tacit assumption is made that there will be future Fischer-Tropsch refineries. The energy security, refining cost and environmental advantages to justify such an assumption have been discussed previously. Once the decision to use Fischer-Tropsch technology has been made, the same change drivers as listed for crude oil refineries apply, although they affect Fischer-Tropsch refineries differently.

a) *Feedstock availability and cost.* Presently all Fischer-Tropsch based facilities use either natural gas or coal as feedstock. Hence, the classification as gas-to-liquids (GTL) or coal-to-liquids (CTL). In principle other feed materials can also be used to produce synthesis gas and in theory biomass-to-liquids (BTL), residue-to-liquids (RTL) and waste-to-liquids

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[nnn] The actual project cost reported in Sasol's interim financial results at the end of 2006 was R 14 750m.

[ooo] The KBR technology claims are interesting from a fundamental point of view. It claims to produce 16% ethylene, 25% propylene, 10% butenes, 2% C_5+ olefins and 24% aromatics (the rest being paraffins, CO, CO_2, water and coke) from a feed that contains about 75% olefins, 5% aromatics, 10% oxygenates and 10% paraffins. Ref. (153) FCC is a carbon rejection technology, yet it results in a product that requires hydrogen rejection.

(WTL) may be considered as options in future.(155) The selection of feedstock determines the operating profitability of the plant, as well as the capital cost. The type of feed material will also influence the gasifier type, which in turn may require the construction of an associated tar refinery. Coal might be seen as one of the options to supplement crude oil for transportation fuel, but tar refineries are not-in-my-backyard (NIMBY) facilities due to their potential environmental impact. At this stage it is not clear which of these materials will be the preferred feedstock for the future, despite the current spate of GTL facilities being planned and constructed.(156) Some of the integration opportunities with crude oil, natural gas, coal pyrolysis products and other feed materials have been discussed elsewhere.(127)

b) *Market demands*. When considering Fischer-Tropsch, the market can potentially be much more than just transportation fuels. The one extreme to consider is a fuels-only refinery and the other extreme is to consider a chemicals-only refinery, like the present Sasol 1 refinery. Combination refinery designs for fuels-and-chemicals can also be considered, like Sasol Synfuels, since Fischer-Tropsch syncrude has significant chemicals potential.(123)(157) Eventually it is market forces and plant location that will favour one design over another, rather than just technical differences.

c) *Refinery and refining cost*. Usually there is trade-off between capital cost and operating cost. In the context of Fischer-Tropsch technology, there are five key decisions that will significantly influence the refinery design and cost: feed stock (GTL or CTL), gasifier type (tar producing or not in the case of CTL), Fisher-Tropsch synthesis (HTFT or LTFT), product slate (fuels, chemicals or both) and market (intermediate or final products). For example, when a refinery produces fuels, the refinery cost can be significantly reduced if only intermediate blending components are produced, like Shell Bintulu and Sasol Oryx. Producing fuels that meet international fuel specifications require a more complex and costly refinery. However, there is always more risk involved in producing intermediate products. There are other cost-benefit parameters to consider in the refinery design too, like future environmental legislation, refinery flexibility, future fuel specifications, availability of capital, market foresight, corporate flexibility (like product exchange with other facilities) and risk aversion. These factors will be discussed in more detail in Chapter VIII.

It should be clear that the factors influencing Fischer-Tropsch refineries are similar to that affecting crude oil refineries, but that the potential diversity that can be introduced by the selection of feed, synthesis gas production, Fischer-Tropsch synthesis and product market, makes it more complex.

10.2. Design of future Fischer-Tropsch refineries

Fischer-Tropsch refining in future and the technology selection for such future refineries is the topic of the second part of this thesis. A detailed analysis of different refining technologies and their compatibility with Fischer-Tropsch syncrude will be made, taking cognisance not only of the technology fit, but also of future fuel specifications and the environmental footprint of the technology. Based on this analysis, specific Fischer-Tropsch refinery designs for the future will be proposed and discussed.

11. Literature cited

(1) Withers, J. G.; West, H. L. *Ruhr-Chemie A.G. Sterkrade Holten interrogation of Dr O Roelen*; British Intelligence Objectives Sub-committee, Final report no.511 Item no.30, Sep 1946.
(2) Weil, B. H.; Lane, J. C. *The technology of the Fischer-Tropsch process*; Constable: London, 1949.
(3) Anderson, R. B.; Krieg, A.; Seligman, B.; O'Neill, W. E. Fischer-Tropsch synthesis. Tests of cobalt catalysts at atmospheric pressure. *Ind. Eng. Chem.* **1947**, *39:12*, 1548.
(4) Asinger, F. *Paraffins chemistry and technology*; Pergamon: Oxford, 1968.
(5) Büssemeier, B.; Frohning, C. D.; Cornils, B. Lower olefins via Fischer-Tropsch. *Hydrocarbon Process.* **1976**, *55:11*, 105.
(6) Freerks, R. *Early efforts to upgrade Fischer-Tropsch reaction products into fuels, lubricants and useful materials*; AIChE Spring National Meeting: New Orleans, USA, 2003, 86d.
(7) Schultz, H., A short history and present trends of Fischer-Tropsch synthesis. *Appl. Catal. A* **1999**, *186*, 3.
(8) Davis, B. H. Overview of reactors for liquid phase Fischer-Tropsch synthesis. *Catal. Today* **2002**, *71*, 249.
(9) Asinger, F. *Mono-olefins chemistry and technology*; Pergamon: Oxford, 1968.
(10) Horne, W. A. Review of German synthetic lubricants. *Ind. Eng. Chem.* **1950**, *42*, 2428.
(11) Snodgrass, C. S.; Perrin, M. The production of Fischer-Tropsch coal spirit and its improvement by cracking. *J. Inst. Petrol. Technologists* **1938**, *24*, 289.

(12) Egloff, G.; Nelson, E. S.; Morrell, J. C. Motor fuel from oil cracking production by the catalytic water gas reaction. *Ind. Eng. Chem.* **1937**, *29*, 555.

(13) Ward, C. C.; Schwartz, F. G.; Adams, N. G. Composition of Fischer-Tropsch diesel fuel. *Ind. Eng. Chem.* **1951**, *43*, 1117.

(14) Seger, F. M.; Doherty, H. G.; Sachanen, A. N. Noncatalytic polymerization of olefins to lubricating oils. *Ind. Eng. Chem.* **1950**, *42*, 2446.

(15) Koch, H.; Ibing, G. Composition of paraffin waxes from the Fischer-Tropsch water-gas synthesis. *Petroleum Refiner* **1943**, *22:9*, 89.

(16) Gall, D. The characteristics of Fischer-Tropsch waxes. *Inst. Petrol. Rev.* **1947**, *1*, 336.

(17) Keith, P. C. Gasoline from natural gas. *Oil Gas J.* **1946**, *45:6*, 102.

(18) Bruner, F. H. Synthetic gasoline from natural gas. Composition and quality. *Ind. Eng. Chem.* **1949**, *41*, 2511.

(19) Steynberg, A. P.; Dry, M. E.; Davis, B. H.; Breman, B. B. Fischer-Tropsch reactors. *Stud. Surf. Sci. Catal.* **2004**, *152*, 64.

(20) Steynberg, A. P. Introduction to Fischer-Tropsch technology. *Stud. Surf. Sci. Catal.* **2004**, *152*, 1.

(21) Anon. Hydrocol process surveyed before WPRA. *Chem. Eng. News* **1947**, *25*, 1044.

(22) Kastens, M. L.; Hirst, L. L.; Dressier, R. G. An American Fischer-Tropsch plant. *Ind. Eng. Chem.* **1952**, *44*, 450.

(23) Alden, R. C. Conversion of natural gas to liquid fuels. *Petroleum Engineer* **1947**, *18:1*, 148.

(24) Helmers, C. J.; Clark, A.; Alden, R. C. Catalytic treatment of synthetic gasoline. *Oil Gas J.* **1948**, *47:26*, 86.

(25) Baird, M. J.; Schehl, R. R.; Haynes, W. P.; Cobb. J. T. Jr Fischer-Tropsch processes investigated at the Pittsburgh energy technology center since 1944. *Ind. Eng. Chem. Prod. Res. Dev.* **1980**, *19*, 175.

(26) Elliot, T. Q.; Goddin, C. S.; Pace, B. S. Chemicals from hydrocarbon synthesis. *Chem. Eng. Progress* **1949**, *45*, 532.

(27) Clark, A.; Andrews, A.; Fleming, H. W. Composition of a synthetic gasoline. *Ind. Eng. Chem.* **1949**, *41*, 1527.

(28) Schlesinger, M. D.; Benson, H. E. Upgrading Fischer-Tropsch products. *Ind. Eng. Chem.* **1955**, *47*, 2104.

(29) Hawley, G. G. *The Condensed Chemical Dictionary*, 8ed; Van Nostrand Reinhold: New York, 1971.

(30) Helmers, C. J.; Brooner, G. M. Catalytic desulfurization and reforming of naphthas over bauxite. *Petroleum Process.* **1948**, *3*, 133.

(31) De Klerk, A. Effect of oxygenates on the oligomerisation of Fischer-Tropsch olefins over amorphous silica-alumina. *Energy Fuels* **2007**, *21*, 625.

(32) McMahon, J. F.; Bednars, C.; Solomon, E. Polymerization of olefins as a refinery process. In *Advances in Petroleum Chemistry and Refining Vol.7*; Kobe, K. A., McKetta, J. J. Eds.; Wiley: New York, 1963, p. 285.

(33) De Klerk, A.; Engelbrecht, D. J.; Boikanyo, H. Oligomerization of Fischer-Tropsch olefins: Effect of feed and operating conditions on hydrogenated motor-gasoline quality. *Ind. Eng. Chem. Res.* **2004**, *43*, 7449.

(34) Tilton, J. A.; Smith, W. M.; Hockberger, W. G. Production of high cetane number diesel fuels by hydrogenation. *Ind. Eng. Chem.* **1948**, *40*, 1269.

(35) Meintjes, J. *Sasol 1950-1975*; Tafelberg: Cape Town, 1975.

(36) Ryan, P. The Synthol process. *Oil Gas J.* **1945**, *43:47*, 264

(37) Jager, B.; Dry, M. E.; Shingles, T.; Steynberg, A. P. Experience with a new type of reactor for Fischer-Tropsch synthesis. *Catal. Lett.* **1990**, *7*, 293.

(38) Dry, M. E. The Fischer-Tropsch synthesis. In *Catalysis Science and Technology Vol.1*; Anderson, J. R., Boudart, M. Eds.; Springer-Verlag: , 1981, p.159.

(39) Dry, M. E. Practical and theoretical aspects of the catalytic Fischer-Tropsch process. *Appl. Catal. A* **1996**, *138*, 319.

(40) Hoogendoorn, J. C. Experience with Fischer-Tropsch synthesis at Sasol. In *Clean Fuels Coal Symp.*; Inst. Gas Technol.: Chicago, 1973, p.353.

(41) Hoogendoorn, J. C.; Salomon, J. M. Sasol: World's largest oil-from-coal plant. II *British Chem. Eng.* **1957**, *Jun*, 308.

(42) Steynberg, A. P.; Espinoza, R. L.; Jager, B.; Vosloo, A. C. High temperature Fischer-Tropsch synthesis in commercial practice. *Appl. Catal. A* **1999**, *186*, 41.

(43) Holtkamp, W. C. A.; Kelly, F. T.; Shingles, T. Circulating fluid bed catalytic reactor for the Fischer-Tropsch synthesis at Sasol II. *ChemSA*, **1977**, *Mar*, 44.

(44) Dry, M. E. FT catalysts. *Stud. Surf. Sci. Catal.* **2004**, *152*, 533.

(45) Dry, M. E. The Sasol Fischer-Tropsch processes. In *Applied Industrial Catalysis Vol. 2*; Leech, B. E. Ed.; Academic Press: New York, 1983, p.167.

(46) Hoogendoorn, J. C. New applications of the Fischer-Tropsch process. In *Clean Fuels Coal Symp., 2nd*; Inst. Gas Technol.: Chicago, 1975, p.343.

(47) Dry, M.E., Sasol's Fischer-Tropsch experience. *Hydrocarbon Process.* **1982**, *61:8*, 121.

(48) Espinoza, R. L.; Steynberg, A. P.; Jager, B.; Vosloo, A. C. Low temperature Fischer-Tropsch synthesis from a Sasol perspective. *Appl. Catal. A* **1999**, *186*, 13.

(49) Hoogendoorn, J. C.; Salomon, J. M. Sasol: World's largest oil-from-coal plant. I *British Chem. Eng.* 1957, *May*, 238.

(50) Ranwell, P.; Van Niekerk, P.; Louw, J. Gasification. In *KGTP*; Sasol: Sasolburg, 1995.

(51) Anon. Gas purification and Arge catalyst production. In *KGTP*; Sasol: Sasolburg, 1995.

(52) Wainwright, H. W.; Kane, L. J.; Wilson, M. W.; Shale, C. C.; Ratway, J. Purification of synthesis gas. Removal of dust, carbon dioxide, and sulfur compounds. *Ind. Eng. Chem.* **1956**, *48*, 1123.

(53) Hochgesand, G. Rectisol and Purisol. *Ind. Eng. Chem.* **1970**, *62:7*, 37.

(54) Weiss, H., Rectisol wash for purification of partial oxidation gases. *Gas Sep. Pur.* **1988**, *2:4*, 171.

(55) Cusumano, J. A.; Dalla Betta, R. A.; Levy, R. B. *Catalysis in coal conversion*; Academic Press: New York, 1978.

(56) Hoogendoorn, J. C.; Salomon, J. M. Sasol: World's largest oil-from-coal plant. IV *British Chem. Eng.* **1957**, *Aug*, 418.

(57) Hoogendoorn, J. C.; Salomon, J. M. Sasol: World's largest oil-from-coal plant. III *British Chem. Eng.* **1957**, *Jul*, 368.

(58) Thomas, J. M.; Thomas, W. J. *Principles and practice of heterogeneous catalysis*; VCH: Weinheim, 1997.

(59) Van Voorhis, M. G. Sohio polymerization unit first using new catalyst. *Nat. Petrol. News* **1940**, *32:26 Jun*, R230.

(60) Wadell, J. D. Finish year's operation of new type of polymerization unit. *Oil Gas J.* **1941**, *28 Aug*, 45.

(61) Armistead, G. Jr Modern refining processes. 5. Nonselective catalytic polymerization has important postwar utility. *Oil Gas J.* **1946**, *44:48*, 131.

(62) Steffens, J. H.; Zimmerman, M. U.; Laituri, M. J. Correlation of operating variables in catalytic polymerization. *Chem. Eng. Progr.* **1949**, *45:4*, 269.

(63) Dazeley, G. H.; Hall, C. C. Production of olefins by the cracking of Fischer-Tropsch waxes and their conversion into lubricating oils. *Fuel* **1948**, *27:2*, 50.

(64) Bolder, F. H. A. Fischer-Tropsch wax hydrogenation over a sulfided nickel-molybdenum catalyst. *Energy Fuels* **2007**, *21*, 1396.

(65) Speight, J. G. *The chemistry and technology of petroleum*, 4ed; CRC Press: Boca Raton, 2007, p.562.

(66) Henley, E. J.; Seader, J. D. *Equilibrium-stage separation operations in chemical engineering*; Wiley: New York, 1981, pp.101-102.

(67) Wessels, P. *Crescendo tot Sukses. Sasol 1975-1987* (Engl. Transl. “Crescendo to success. Sasol 1975-1987”); Human & Rousseau: Cape Town, 1990.

(68) Dry, M. E. High yield high quality diesel from Fischer-Tropsch process. *ChemSA* **1984**, *10:2*, 286.

(69) Hoogendoorn, J. C. Producing automotive fuels from coal in South Africa. *Hydrocarbon Process.* **1982**, *61:5*, 34E.

(70) Joiner, J. R.; Kovach, J. J. Sasol Two and Sasol Three. *Energy Progr.* **1982**, *2:2*, 66.

(71) Linnig, D. A.; Mako, P. F.; Samuel, W. A. Coal to oil and gas. Sasol One, Two, and Three. *Energy Process. Canada* **1982**, *74:1*, 49.

(72) Kronseder, J. G.; Bogart, M. J. P. Coal, liquefaction, South Africa's Sasol II. *Encycl. Chem. Process. Des.* **1979**, *9*, 299.

(73) Dry, M. E. Chemicals produced in a commercial Fischer-Tropsch process. *ACS Symp. Ser.* **1987**, *328*, 18.

(74) Marriott, J. N. Sasol process technology - the challenge of synfuels from coal. ChemSA 1986, 12:8, 174.

(75) Collings, J. *Mind over matter. The Sasol story: A half-century of technological innovation*; Sasol: Johannesburg, 2002.

(76) Rossouw, A. *Gas Liquor Separation (U 13) and Raw Gas Cooling (U 11)*; Sasol internal presentation, 2004.

(77) Fenton, D. M.; Gowdy, H. W. The chemistry of the Beavon sulfur removal process. *Environ. Int.* **1979**, *2:3*, 183.

(78) Vermaire, S.; De Haan, R. Influence of sodium carbonate/vanadium concentration ratios on vanadate (V) equilibria and on the reoxidation of V(IV) in a hydrogen sulfide removal process. *Ind. Eng. Chem. Res.* **1988**, *27*, 1242.

(79) Jhanji, A. K.; Carrano, C. J. Vanadium(V) complexes of sulfonated 1,5,10-tris(2,3-dihydroxybenzoyl)-1,5,10-triazadecane as catalysts for the Stretford process. *Inorg. Chim. Acta* **1993**, *214*, 141.

(80) Aasberg-Petersen, K.; Christensen, T. S.; Dybkjær, I.; Sehested, J.; Østberg, M.; Coertzen, R. M.; Keyser, M. J.; Steynberg, A. P. Synthesis gas production for FT synthesis. *Stud. Surf. Sci. Catal.* **2004**, *152*, 258.

(81) Bartoo, R. K. Removing acid gas by the Benfield process. *Chem. Eng. Prog.* **1984**, *80:10*, 35.

(82) Sanyal, D.; Vasishtha, N.; Saraf, D. N. Modeling of carbon dioxide absorber using hot carbonate process. *Ind. Eng. Chem. Res.* **1988**, *27*, 2149.

(83) Chauvel, A.; Lefebvre, G. *Petrochemical Processes. 1. Synthesis-gas derivatives and major hydrocarbons*; Technip: Paris, 1989, pp.149-154.

(84) Van Zyl, J. S. *Sasol Synfuels Refinery Units*; Sasol internal communication, 2003.

(85) Leckel, D. O. Catalytic hydroprocessing of coal-derived gasification residues to fuel blending stocks: Effect of reaction variable and catalyst on hydrodeoxygenation (HDO), hydrodenitrogenation (HDN), and hydrodesulfurization (HDS). *Energy Fuels* **2006**, 20, 1761.

(86) Swart, J. S.; Czajkowski, G. J.; Conser, R. E. Sasol upgrades Synfuels with refining technology. Oil Gas J. 1981, 79:35, 62.

(87) De Klerk, A. Refining of Fischer-Tropsch syncrude: Is it more environmentally friendly than refining crude oil? *Prepr. Am. Chem. Soc. Div. Fuel Chem.* **2006**, *51:2*, 704.

(88) Langlois, G. E.; Walkey, J. E. Improved process polymerizes olefins for high-quality gasoline. *Petroleum Refiner* **1952**, *31:8*, 79.

(89) McMahon, J. F.; Bednars, C.; Solomon, E. Polymerization of olefins as a refinery process. Kobe, K. A.; McKetta, J. J. (eds) *Advances in Petroleum Chemistry and Refining Vol.7*; Wiley: New York, 1963, 285.

(90) Prinsloo, N. M. Solid phosphoric acid oligomerisation: Manipulating diesel selectivity by controlling catalyst hydration. *Fuel Process. Technol.* **2006**, *87*, 437.

(91) De Klerk, A.; Leckel, D. O.; Prinsloo, N. M. Butene Oligomerisation by Phosphoric Acid catalysis: Separating the effects of temperature and catalyst hydration on product selectivity. *Ind. Eng. Chem. Res.* **2006**, *45*, 6127.

(92) Weinert, P. C.; Egloff, G. Catalytic polymerization and its commercial application. *Petroleum Process.* **1948**, *June*, 585.

(93) Deeter, W. F. Propene polymerization for motor-gasoline production. *Oil Gas J.* **1950**, *23 March*, 252.

(94) Ipatieff, V. N.; Schaad, R. E. Mixed polymerization of butenes by solid phosphoric acid catalyst. *Ind. Eng. Chem.* **1938**, *30*, 596.

(95) Roux, F. *Chemical and physical properties of selected SSF and Natref fuel components*, issue 5; Sasol internal communication, 2001.

(96) Bolder, F. H. A.; Mulder, H. Dehydration of alcohols in the presence of carbonyl compounds and carboxylic acids in a Fischer-Tropsch hydrocarbons matrix. *Appl. Catal. A* **2006**, *300*, 36.

(97) Antos, G. J.; Aitani, A. M. (eds) *Catalytic naphtha reforming*; Marcel Dekker: New York, 2004.

(98) Lapinski, M.; Baird, L.; James, R. UOP Platforming process. In *Handbook of Petroleum Refining Processes*; Meyers, R.A. (ed); McGraw-Hill: New York, 2004, 4.3.

(99) Wei, D. H.; Moser, M. D.; Haizmann, R. S. An update on catalytic reforming. *Chemtech* **1996**, *Oct*, 37.

(100) Terblanche, K. The Mossgas challenge. *Hydrocarbon Eng.* **1997**, *Mar*, 2.

(101) Naidoo, N. *Trends in the South African oil industry*; 2nd Sub-Saharan Africa Catal. Symp.: Swakopmund, Namibia, 2001.

(102) Steyn, C. *The role of Mossgas in Southern Africa*; 2nd Sub-Saharan Africa Catal. Symp.: Swakopmund, Namibia, 2001.

(103) Travers, C. Isomerization of light paraffins. In *Petroleum Refining Vol.3 Conversion Processes*; Leprince, P. Ed.; Editions Technip: Paris, 2001, p.229.

(104) Corma, A.; Martínez, A. Chemistry, catalysts, and processes for isoparaffin-olefin alkylation. Actual situation and future trends. *Catal. Rev.-Sci. Eng.* **1993**, *35*, 483.

(105) Köhler, E.; Schmidt, F.; Wernicke, H. J.; De Pontes, M.; Roberts, H. L. Converting olefins to diesel - the COD process, *Hydrocarbon Technol. Int.* **1995**, *Summer*, 37.

(106) Quann, R. J.; Green, L. A.; Tabak, S. A.; Krambeck, F. J. Chemistry of olefin oligomerization over ZSM-5 catalyst. *Ind. Eng. Chem. Res.* **1988**, *27*, 565.

(107) Minnie, O. R.; Petersen, F. W.; Samadi, F. R. *Effect of 1-hexene extraction on the COD process conversion of olefins to distillate*; South African Chem. Eng. Congr.: Sun City, South Africa, 2003.

(108) Minnie, O. R. *The effect of 1-hexene extraction on the COD process*; MTech dissertation, University of South Africa (Pretoria, South Africa), 2006.

(109) Knottenbelt, C. Mossgas "gas-to-liquids" diesel fuels - an environmentally friendly option. *Catal. Today* **2002**, *71*, 437.

(110) De Klerk, A. Properties of synthetic fuels from H-ZSM-5 oligomerisation of Fischer-Tropsch type feed materials. *Energy Fuels* **2007**, *21*, 3084.

(111) Cusher, N. A. UOP Penex process. In *Handbook of Petroleum Refining Processes*; Meyers, R.A. (ed); McGraw-Hill: New York, 2004, pp.9.15.

(112) Nel, R. J. J.; De Klerk, A. Fischer-Tropsch aqueous phase refining by catalytic alcohol dehydration. *Ind. Eng. Chem. Res.* **2007**, *46*, 3558.

(113) Smith, R.; Asaro, M. *Fuels of the future. Technology intelligence for gas to liquids strategies*; SRI: Menlo Park, CA, 2005.

(114) Sie, S. T. Process development and scale-up. IV. Case history of the development of a Fischer-Tropsch synthesis process. *Rev. Chem. Eng.* **1998**, *14:2*, 109.

(115) Sie, S. T.; Senden, M. M. G.; Van Wechem, H. M. W. Conversion of natural gas to transportation fuels via the Shell Middle Distillate Synthesis process (SMDS). *Catal. Today* **1991**, *8*, 371.

(116) Schrauwen, F. J. M. Shell Middle Distillate Synthesis (SMDS) process. In *Handbook of Petroleum Refining Processes*; Meyers, R.A. (ed); McGraw-Hill: New York, 2004, pp.15.25.

(117) Eilers, J.; Posthuma, S. A.; Sie, S. T. The Shell middle distillate synthesis process (SMDS). *Catal. Lett.* **1990**, *7*, 253.

(118) Reinalda, D.; Blankenstein, P. Process for the preparation of zirconia-based catalyst, US Patent 5,217,938 (8 Jun 1993).

(119) Tijm, P. J. A.; Van Wechem, H. M. H.; Senden, M. M. G. *The Shell Middle Distillate Synthesis project new opportunities for marketing natural gas*; Alternate Energy '93 Conference, Colorado Springs, USA, 1993, 27-30 April.

(120) Daya, A. In vogue. *Petroleum Economist* **2006**, *73:4*, 27.

(121) Anon. Oryx plant produces GTL products for first time. *Oil Gas J.* **2007**, *105:5*, 10.

(122) Forbes, A. Reality check. *Petroleum Economist* **2007**, *74:7*, 30.

(123) Steynberg, A. P.; Nel, W. U.; Desmet, M. A. Large scale production of high value hydrocarbons using Fischer-Tropsch technology. *Stud. Surf. Sci. Catal.* **2004**, *147*, 37.

(124) Forbes, A. Surge in interest a long time coming. *Petroleum Economist* **2007**, *74:1*, 19.

(125) Halstead, K. Oryx GTL - a case study. *Chemical Technology (S. Afr.)* **2006**, *Nov*, 28.

(126) Dry, M. E.; Steynberg, A. P. Commercial FT process applications. *Stud. Surf. Sci. Catal.* **2004**, *152*, 406.

(127) Dancuart, L. P.; De Haan, R.; De Klerk, A. Processing of primary Fischer-Tropsch products. *Stud. Surf. Sci. Catal.* **2004**, *152*, 482.

(128) Dancuart, L. P.; Mayer, J. F.; Tallman, M. J.; Adams, J. Performance of the Sasol SPD naphtha as steam cracking feedstock. *Prepr. Am. Chem. Soc. Div. Pet. Chem.* **2003**, *48:2*, 132.

(129) Lamprecht, D.; Roets, P. P. N. J. Sasol Slurry Phase Distillate™ semi-synthetic aviation turbine fuel. *Prepr. Am. Chem. Soc. Div. Pet. Chem.* **2004**, *49:4*, 426.

(130) Anon. Gaint Project Turbo advances. *Chemical Technology (S. Afr.)* **2005**, *Oct*, 13.

(131) Mashapa, T. N.; Rademan, J. D.; Janse van Vuuren, M. J. Catalytic performance and deactivation of precipitated iron catalyst for selective oxidation of hydrogen sulfide to

elemental sulfur in the waste gas streams from coal gasification. *Ind. Eng. Chem. Res.* **2007**, *46*, 6338.

(132) Dancuart, L. P.; Steynberg, A. P. Fischer-Tropsch based GTL technology: a new process? *Stud. Surf. Sci. Catal.* **2007**, *163*, 379.

(133) Luyt, A. S. *Die oksidasiekinetika van 'n Fischer-Tropsch-was* (Engl. Transl. "The oxidation kinetics of a Fischer-Tropsch wax"); PhD thesis, Potchefstroom University for Christian Higher Education, 1985.

(134) De Klerk, A., Continuous-mode thermal oxidation of Fischer-Tropsch waxes. *Ind. Eng. Chem. Res.* **2003**, *42*, 6545.

(135) Lund, G.; Davis, W.; Coogan, E.; De Wit, G.; Naidoo, R. Extraction of tar acids from naphtha streams: Tar Naphtha Phenolic Extraction (TNPE) plant. *Chemical Technology (S. Afr.)* **2006**, *Dec*, 10.

(136) Nicol, W.; Du Toit, E. L. One-step methyl isobutyl ketone synthesis from acetone and hydrogen using Amberlyst CH28. *Chem. Eng. Process.* **2004**, *43*, 1539.

(137) Chauvin, Y.; Gaillard, J.; Léonard, J.; Bonnifay, P.; Andrews, J. W. Another use for Dimersol. *Hydrocarbon Process.* **1982**, *61:5*, 110.

(138) Camara Greiner, E. O.; Gubler, R.; Inoguchi, Y. *Chemical Economics Handbook Marketing Research Report: Linear Alpha Olefins* (May 2004); SRI: Menlo Park, 2004.

(139) *Process Economics Program Report 12D, Linear Alpha Olefins*; SRI: Menlo Park, 2001.

(140) De Klerk, A. Etherification of C_6 Fischer-Tropsch material for linear α-olefin recovery. *Ind. Eng. Chem. Res.* **2004**, *43*, 6349.

(141) Joubert, D. J.; Tincul, I. Ethylene copolymers with Fischer-Tropsch olefins. *Macromolecular Symp.* **2002**, *178*, 69.

(142) Wahner, U. M.; Tincul, I.; Joubert, D. J.; Sadiku, E. R.; Fortini, F.; Losio, S.; Tritto, I.; Sacchi, M. C. ^{13}C NMR study of copolymers of propene with higher 1-olefins with new microstructures by ansa-zirconocene catalysts. *Macromolecular Chem. Phys.* **2003**, *204*, 1738.

(143) Diamond, D.; Hahn, T.; Becker, H.; Patterson, G. Improving the understanding of a novel complex azeotropic distillation process using a simplified graphical model and simulation. *Chem. Eng. Process.* **2004**, *43*, 483.

(144) McGurk, K. *From 1-heptene to 1-octene: A new production route*; South African Chemical Engineering Congress: Sun City, South Africa, 2003.

(145) Beller, M.; Cornils, B.; Frohning, C. D.; Kohlpaintner, C. W. Progress in hydroformylation and carbonylation. *J. Mol. Catal. A* **1995**, *104*, 17.

(146) Redman, A. *Production of olefins and oxygenated compounds from Fischer-Tropsch*; 18th World Petroleum Congress: Johannesburg, South Africa, 2005.

(147) Colley, S. W.; Tuck, M. W. M. Ethyl ethanoate synthesis by ethanol dehydrogenation. In *Catalysis in application*; Jackson, S. D., Hargreaves, J. S. J., Lennon, D. Eds.; Royal Society of Chemistry: Cambridge, 2003, p.101.

(148) Ignatius, J.; Järvelin, H.; Lindqvist, P. Use TAME and heavier ethers to improve gasoline properties. *Hydrocarbon Process.* **1995**, *74:2*, 51.

(149) Duplan, J-L.; Amigues, P.; Verstraete, J.; Travers, C. Kinetic studies of the skeletal isomerization of n-pentenes over the ISO-5 process catalyst. *Proc. Ethylene Prod. Conf.* **1996**, *5*, 429.

(150) Van Wyk, A. M.; Moola, M. A.; De Bruyn, C. J.; Venter, E.; Collier, L. Molecule management for clean fuels at Sasol. *Chemical Technology (S. Afr.)* **2007**, *Apr*, 4.

(151) Len, A. S.; Pavone, T. An alternative option for producing light olefins. *Petroleum Technol. Quarterly* **2004**, *9:1*, 89.

(152) Eng, C.; Heidenreich, S.; Swart, S.; Möller, F. *Clean fuels and petrochemicals at Sasol via Superflex*™; 18th World Petroleum Congress: Johannesburg, South Africa, 2005.

(153) Brack, B. Superflex pilot plant evaluation at KBR using SSF C_6/C_7 feed, Report PDR/04/0144, 1 Nov 2004; *Sasol technology internal communication*.

(154) De Klerk, A. Distillate production by oligomerization of Fischer-Tropsch olefins over Solid Phosphoric Acid. *Energy Fuels* **2006**, *20*, 439.

(155) Peckham, J. New center emerging for advanced gasification: Biomass, waste, coal-to-liquids for fuels, power. *World Refining* **2005**, *15:4*, 18.

(156) Quinlan, M. New product hits the road. *Petroleum Economist* **2006**, *73:6*, 7.

(157) De Klerk, A.; Dancuart, L. P.; Leckel, D. O. *Chemicals refining from Fischer-Tropsch synthesis*; 18th World Petroleum Congress: Johannesburg, South Africa, 2005, cd185.