Motor Fuels and Chemicals from Coal Via the Sasol Synthol Route [and Discussion]

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Motor fuels and chemicals from coal via the Sasol Synthol route

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The production of motor fuels and chemicals from coal is based on the Fischer–Tropsch reaction by passing hydrogen and carbon monoxide in a specific ratio over iron catalysts at elevated temperatures and pressures.

The fixed-bed system employs a precipitated iron catalyst. Predominantly heavy hydrocarbons of an aliphatic nature are produced with carbon chains up to 100. These straight-chain hydrocarbons yield excellent waxes and high quality diesel oil, which is also used as raw material for the production of very high quality biodegradable detergents.

The fluid-bed system, based on catalytic cracker technology, has the great advantage of high production capacity and scale-up potential. Scaled-up reactors are the only ones used at Sasol Two and Sasol Three. The quantity of ethylene obtained is augmented by ethane cracking. The light olefins can be used as petrochemical feedstock or refined, e.g. by polymerization, and the product added to the motor fuel pool. The product cut in the gasoline range yields a good quality gasoline by using conventional refinery techniques. The oxygenated chemicals, when sold as such, fetch higher prices than when sold as motor fuels.

1. BACKGROUND

Sasol, formerly known as The South African Coal, Oil and Gas Corporation, started producing synthetic motor fuels from coal on a commercial scale more than 25 years ago. A number of papers on the plant and processes employed have been published. For the purpose of this paper, however, it is sufficient to mention that the original operations that started production during 1955 consisted of Lurgi coal gasification followed by Lurgi Rectisol gas purification, producing a synthesis gas of very high purity, consisting mainly of hydrogen and carbon monoxide in the ratio required for the following synthesis reactions and also some methane. Hydrocarbons are synthesized from this gas by the Fischer–Tropsch reaction which in a very simplified form can be given as

$$2n\mathrm{H_2} + n\mathrm{CO} \longrightarrow (\mathrm{CH_2})_n + n\mathrm{H_2O}.$$

Hydrocarbons of a wide range of molecular masses are formed, the range depending on catalyst properties and also on reaction conditions. The hydrocarbons are mainly olefins and paraffins. Under the reaction conditions, some of the olefins may be hydrated or oxidized. A simple example is the formation of ethanol:

$$\mathrm{C_2H_4} + \mathrm{H_2O} \longrightarrow \mathrm{C_2H_5OH}.$$

In the original plant in Sasolburg, now known as Sasol One, two parallel reactor systems were used; they are still in use today. The smaller system employs fixed-bed reactors, using a precipitated iron catalyst. This system was originally developed by the two German companies, Lurgi and Ruhrchemie, as a continuation of the German World War II technology.

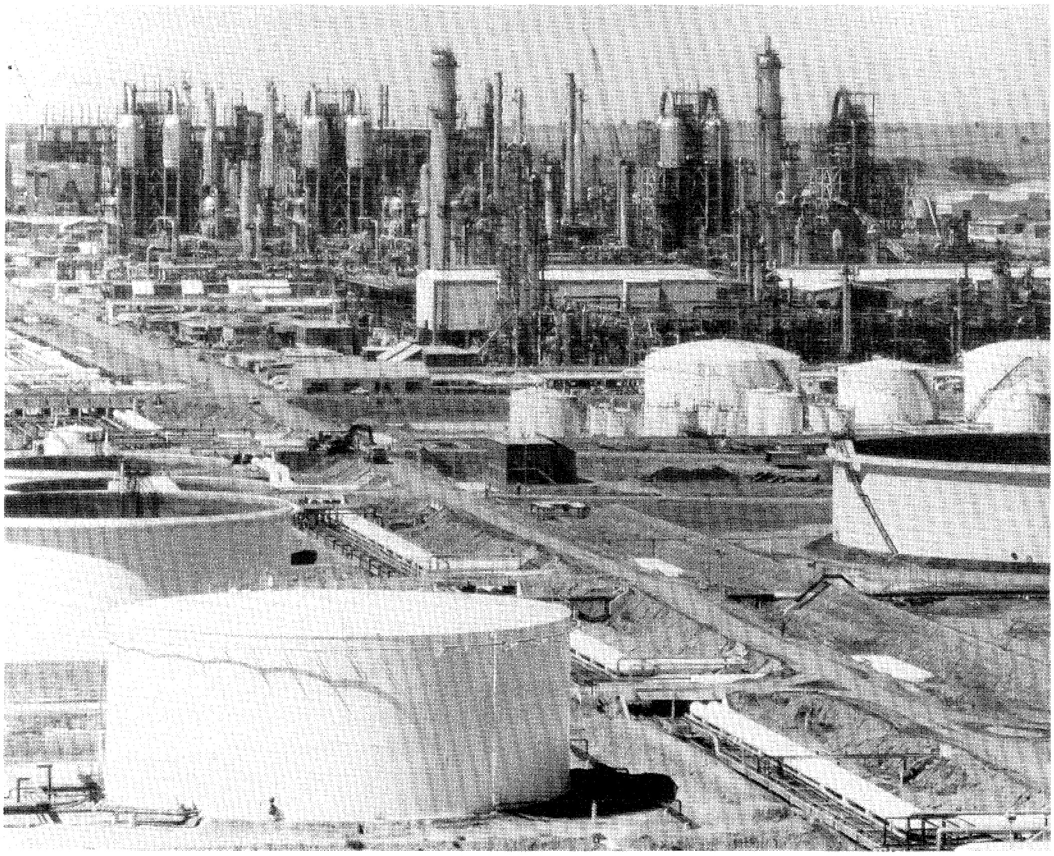

Figure 1. Synthol reactors of Sasol One.

The larger system uses a powdered iron catalyst in a circulating fluid-bed reactor, a concept developed from American catalytic cracker technology. Originally two reactors were built. After commissioning, it appeared that there were wide gaps between the available data from the small pilot plant on which the design was based and the actual information needed to operate a commercial size reactor, and Sasol had to spend much research and engineering (and lots of money) before the potential of this system could be used to the full extent. These expensive but valuable lessons have, however, borne fruit and today the Sasol Synthol fluid-bed reactor system is a highly reliable system with predictable behaviour. Three reactors are now in operation. Figure 1 shows the three reactors in the foreground and figure 2 gives a general view of Sasol One.

2. The fixed-bed system

The fixed-bed system can be operated in such a way that predominantly heavy hydrocarbons are produced, highly paraffinic in nature and with carbon chains of up to 100. These straight-chain hydrocarbons yield excellent waxes which can find their way into industry, either as the waxes themselves or modified by oxidation, esterification, etc. Application fields are the paper and packaging industry, textile industry, food industry, printing materials, etc. The middle distillates from this reactor system have, owing to their straight-chain character, excellent properties as diesel fuel, but at the same time they offer an interesting starting material for biodegradable detergents. The hydrocarbons in the gasoline range have low octane values and

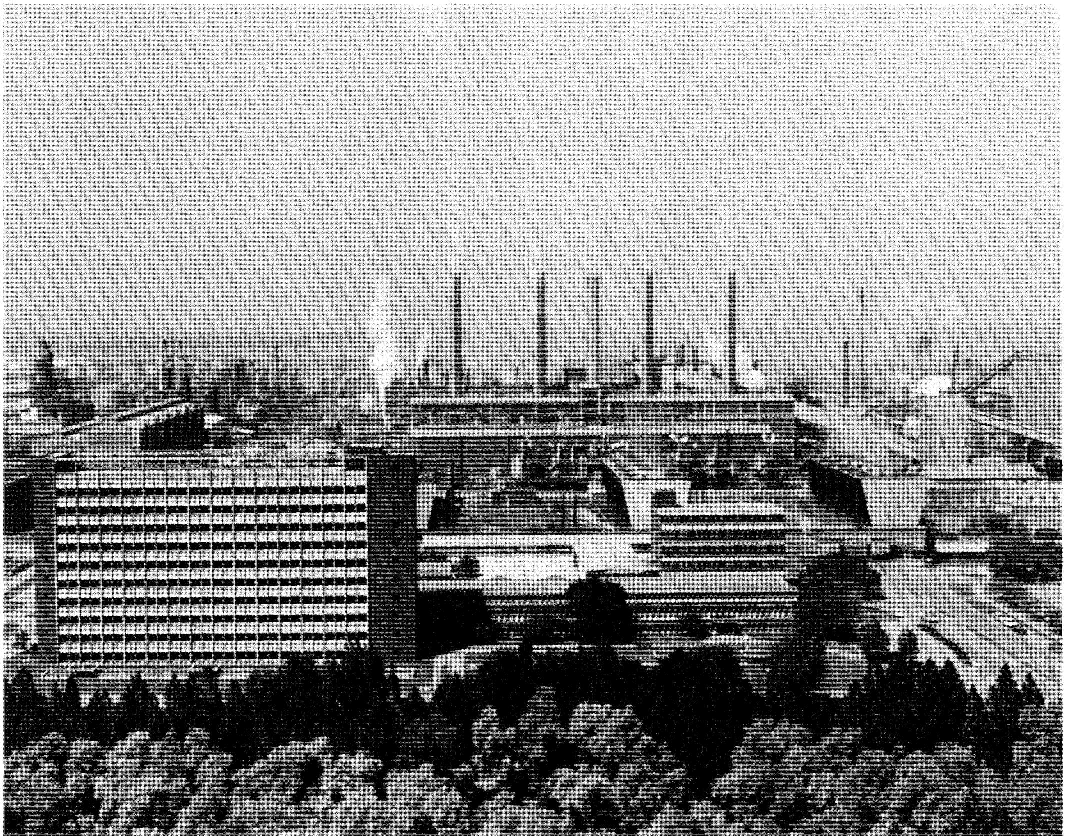

Figure 2. General view of Sasol One.

would require considerable refining and upgrading to become gasoline in their own right. However, the volume is small and in the Sasolburg operations this fraction can easily be blended away.

3. The fluid-bed system

The fluid-bed Synthol reactor system has the great advantages of high capacity and scale-up potential. To maintain the fluidization properties of the catalyst, it is of course necessary to avoid production of waxy hydrocarbons in this reactor and conditions are chosen to operate this system basically as a producer of light motor fuels and oxygenates. The products are more branched and some aromatics are formed. High yields of hydrocarbons in the gasoline range, when subjected to the normal refining procedures, yield a high quality gasoline which need not be upgraded by the addition of blending stocks. The diesel oil fraction is also of good quality.

4. Sasol Two

In 1974, with the sharp increase in oil prices, the construction of another Sasol plant of a much larger capacity with motor fuel as the main product became economically viable in South Africa. The decision to use scaled-up Synthol reactors was obvious. Figure 3 shows some of the reactors as erected at Sasol Two and figure 4 gives a general view of the works.

In the design of this Sasol Two plant, full use was made of all the experience gained in the

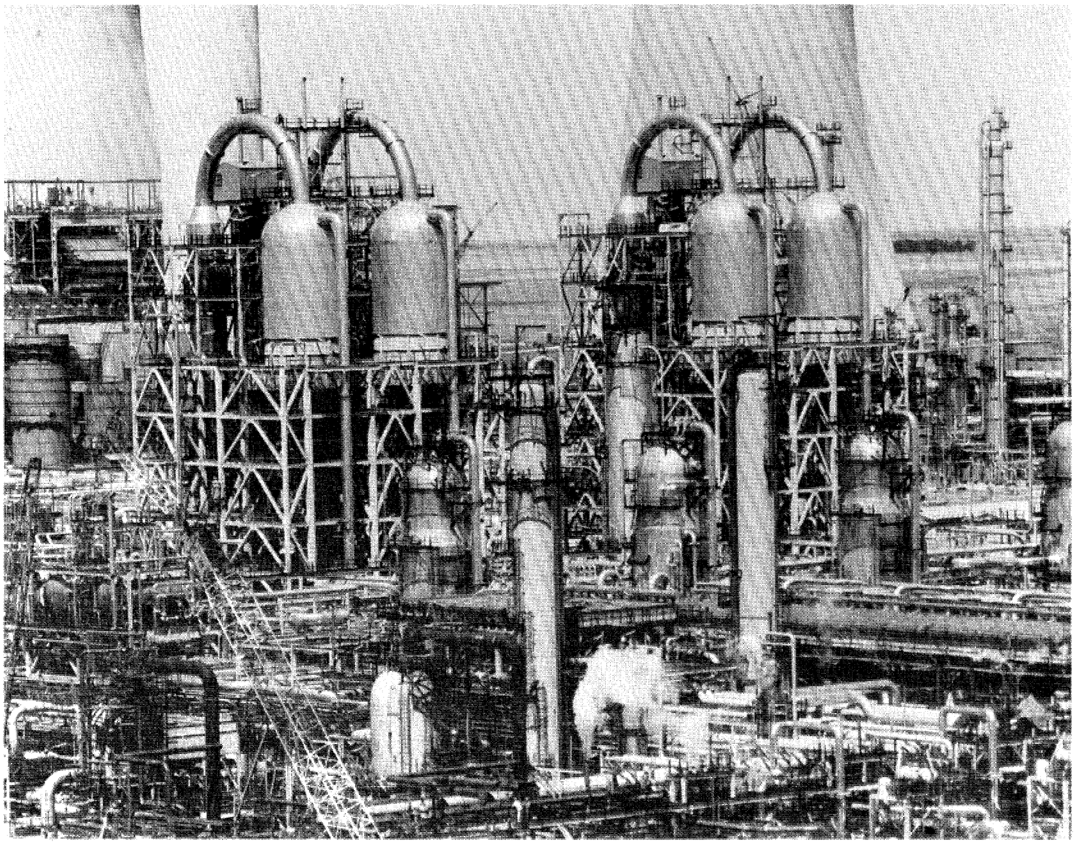

FIGURE 3. Synthol reactor of Sasol Two.

Sasol One operations from coal handling up to refining and product despatch. This experience includes not only operation but also maintenance techniques, choice of material of construction, and design improvements. Though Sasol Two has a much larger capacity than Sasol One, the flowsheet is really much simpler because only one Fischer–Tropsch system is used. For comparison, the simplified flowsheets of Sasol One and Sasol Two are given in figures 5 and 6.

Methane, formed in the gasification process, plus a smaller amount of methane synthesized by the Fischer–Tropsch reaction, is concentrated in the tailgas of the reactors and reformed back to synthesis gas; alternatively, the tailgas, which has a heating value of 20 MJ/m^3 at s.t.p., can be used as pipeline gas. In Sasol One this is the normal operation and reforming is done only over weekends when pipeline gas demands are low. Light hydrocarbons are recovered from the tailgas in an oil absorption system.

In the Sasol Two plant, the tailgas, after recovery of the condensable hydrocarbons, is routed to a low-temperature separation plant which not only gives a very high recovery of the C_3 and C_4 hydrocarbons but also separates a C_2 stream and a methane stream with a concentration of approximately 90 %. The mixed ethylene–ethane stream is used for ethylene production in an ethane cracker. The methane stream is again reformed by partial oxidation to synthesis gas for recycling to the Synthol reactors. With the increasing demand for pipeline gas, the methane stream could be diverted into the pipeline system. If a need for pipeline gas (s.n.g.) exists, then the reforming plant can of course be completely eliminated and an even simpler flowsheet will

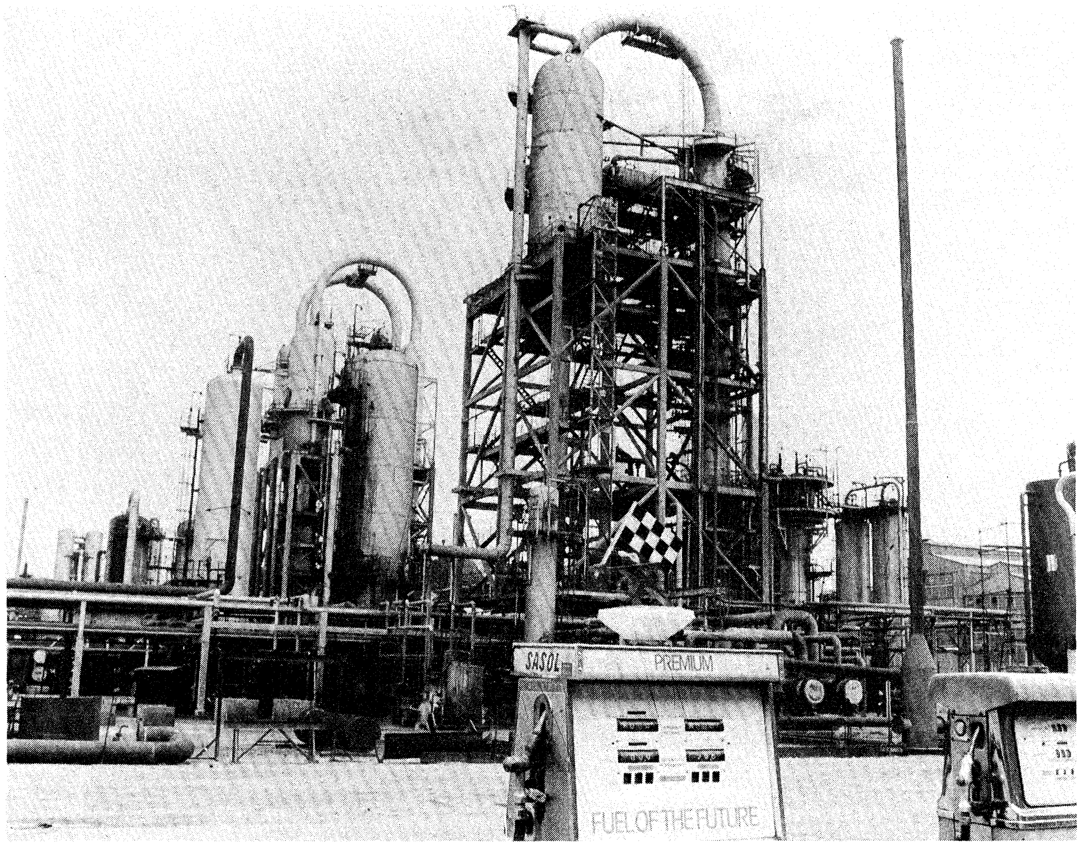

Figure 4. General view of Sasol Two.

result (figure 7). This is a type of operation which for instance would apply under American conditions where a need for liquid fuels as well as s.n.g. exists. It should be noted that the greater part of the methane in the tailgas from the Synthol reactors originates from the gasification process and if a methane-free feedgas were used, the amount of methane in the tailgas would be substantially lower and a smaller reforming section would be required. However, production of methane-free gas from coal is in general thermally less efficient, essentially because the reforming reaction then takes place under less favourable conditions in the gasifier itself, resulting in a higher oxygen consumption. Obviously the economical optimum configuration of processes will vary with the location of the plants and the availability of markets for the products and their prices.

The same applies to the by-products of gasification, which, if produced on a large scale as in the Sasol plants, fully justify recovery and refining to produce additional valuable fuels and industrial products.

5. Product selectivities

For a good understanding of the potential of the Fischer–Tropsch system for production of chemicals in parallel with motor fuels, it is of interest to compare some possible ranges of product selectivities obtained under different operating conditions and with different catalyst variations. Table 1 shows selectivities for commercial Sasol Synthol operation, commercial

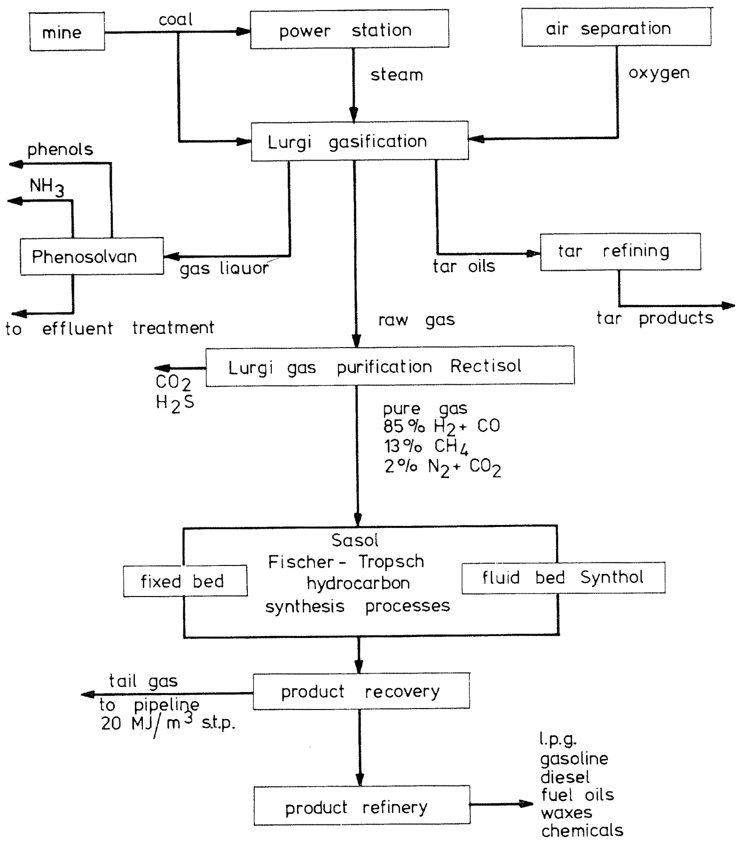

FIGURE 5. Sasol Synthol process: simplified flowsheet for Sasol One.

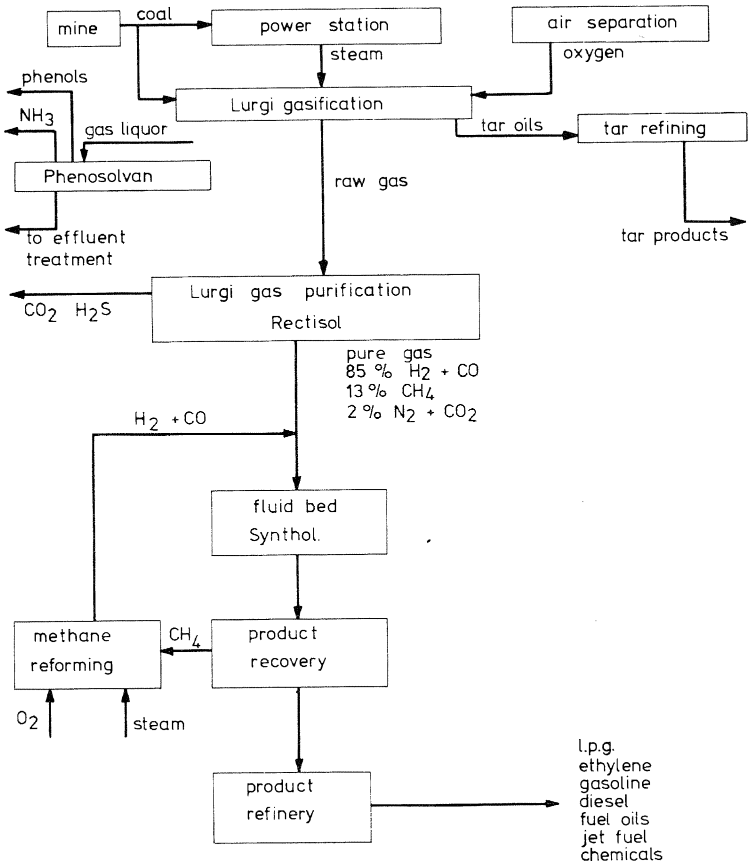

FIGURE 6. Sasol Synthol process: simplified flowsheet for Sasol Two.

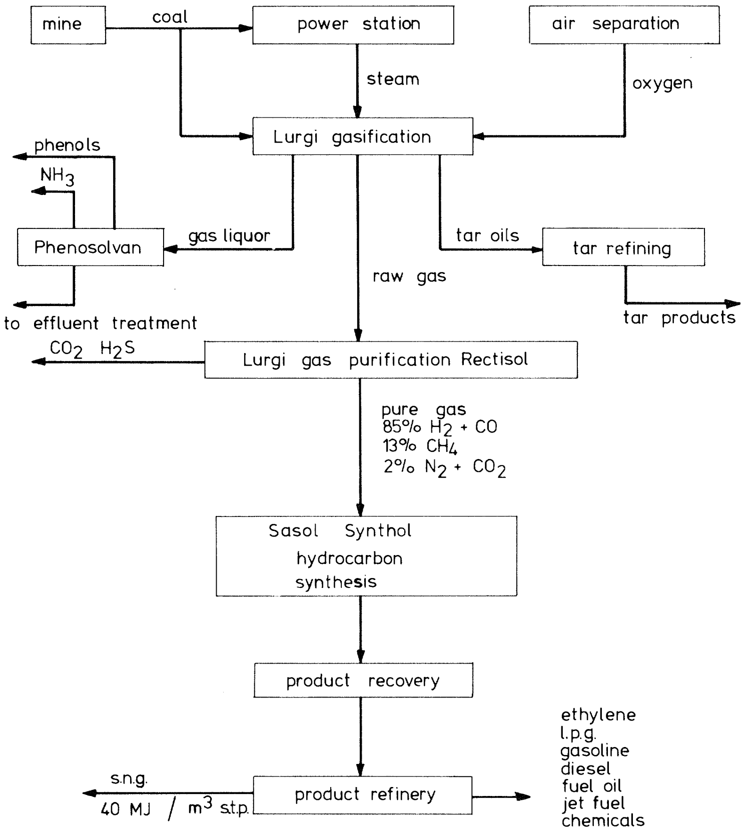

FIGURE 7. Sasol Synthol process: production of motor fuels and s.n.g.

TABLE 1. PRODUCT SELECTIVITIES

product	commercial Synthol	experimental	commercial fixed-bed
CH_4	10	14	2.0
C_2H_4	4	9	0.1
C_2H_6	4	4	1.8
C_3H_6	12	13	2.7
C_3H_8	2	3	1.7
C_4H_8	9	11	3.1
C_4H_{10}	2	2	1.9
$\geqslant C_5$	51	44	83.5
soluble chemicals	5	—	3.0
water soluble acids	1	—	0.2

fixed-bed operation and an experimentally obtained selectivity where the objective was to increase the volume of light olefins.

In all three cases promoted iron catalysts were used. These catalysts are known to have satisfactory lives. It should also be noted that though different reactor systems are compared, the reactor system itself has only a minor influence on the results if operated under similar conditions but as the Fischer–Tropsch reaction is highly exothermic, the reactor design and the speed with which heat of reaction can be removed may put a restriction on the reaction conditions used. This table shows clearly that the commercial Synthol operation affords the opportunity to obtain appreciable amounts of light olefins as a separate product stream for chemical feedstock which could be refined, e.g. by polymerization, and the product added to the motor fuel pool.

TABLE 2. PROPERTIES OF HYDROCARBONS IN THE GASOLINE RANGE

product cut	composition	fixed-bed	Synthol
gasoline C_5–C_{11}	olefins	32	65
	paraffins (total)	60	14
	n-paraffins	57	8
	aromatics	0	7
	alcohols	7	6
	ketones	0.6	6
	acids	0.4	2
	r.o.n. (Pb-free)	*ca.* 35	88

Table 2 shows some properties of the reactor products in the gasoline range obtained under different conditions. The fluid-bed product is much higher in olefins and also contains aromatics in the gasoline fraction. In the fixed-bed products, however, aromatics are absent and the olefin fraction much smaller. The paraffins are predominantly straight chain. The difference in composition is clearly illustrated by the lead-free octane numbers. Table 3 gives the same comparison for the diesel fraction and here of course the same difference in basic properties results in a higher cetane number for the fixed-bed product.

TABLE 3. PROPERTIES OF HYDROCARBONS IN THE DIESEL RANGE

product cut	composition	fixed-bed	Synthol
diesel C_{12}–C_{18}	olefins	25	73
	paraffins (total)	65	10
	n-paraffins	61	6
	aromatics	0	10
	alcohols	6	4
	ketones	1	2
	acids	0.05	1
	cetane number	*ca.* 65	50

The water soluble non-acid chemicals from the Synthol process consist basically of alcohols and ketones with small quantities of aldehydes. After hydrogenation of the aldehydes, these chemicals can be split into commercial fractions. Ethanol constitutes more than half of the total product. Commercial products sold by Sasol include industrial ethanol, propanol, butanol, acetone, MEK and mixed higher alcohols. On the other hand, if the objective is to produce maximum motor fuel, then one could simply separate ketones and alcohols, and use the ethanol and higher alcohol mixture as an additive to gasoline. The presence of the higher alcohols in such a mixture has advantages as it decreases the risk of phase separation when the mixture becomes contaminated with water.

6. VALUE OF PRODUCTS

We can now try to quantify differences in income between the case where all products from the synthesis can find their own market and the case where no chemical market exists and only motor fuels are produced.

Table 4 shows the case for full-product values. A selectivity is assumed similar to a typical commercial Synthol operation. The unit values used are typical for published prices during the first quarter of 1980. The methane value is based on a landed l.n.g. price of $3 per 10^6 Btu (1.055 GJ). The oxygenated chemicals are for convenience taken as ethanol. Ethane has been given a value that would justify its cracking to produce ethylene. The refined fraction over C_5 has been given an average value of gasoline and diesel. The total value of this product packet is approximately $36000.

Table 4. Product values: motor fuels and chemicals

	mass units	unit price/($/ton†)	total price/$
CH_4	10	160	1600
C_2H_4	4	750	3000
C_2H_6	4	400	1600
C_3H_6	12	500	6000
C_3H_8	2	340	4400
C_4H_8	9		
C_4H_{10}	2		
$\geqslant C_5$	51	340	17300
‘C_2H_5OH’	5	500	2500
total	**99**		**36400**

† 1 U.S. ton = 0.9072 t.

Let us consider the case where only motor fuels can be marketed and where the methane and the full C_2 fractions are reformed to synthesis gas which is recycled to the Synthol reactors (table 5).

Table 5. Product values: motor fuels only

	mass units	unit price/($/ton)	total price/$
CH_4	0		
C_2H_4	0		
C_2H_6	0		
C_3H_6	14	340	29200
C_3H_8	2		
C_4H_8	10		
C_4H_{10}	2		
$\geqslant C_5$	58		
‘C_2H_5OH’	6	200	1200
total	**92**		**30400**

The reforming is an unavoidable thermal loss and the net result is that the total volume of products drops from an equivalent 99 C atoms in the full case to 92 C atoms in this case. The motor fuels are assigned the same sales value as in the previous table, but the value of the ethanol has now been corrected for its lower energy content. The result is a total product value of about $30000, or approximately 85% of the original value. There is of course also a difference in capital cost of the two plants. For motor fuels the low temperature light hydrocarbon recovery plant with the ethylene purification unit can be omitted and replaced by a cheaper oil absorption unit to recover the useful light hydrocarbons. The recovery plant for the chemical fractions is also simpler and cheaper, but now a reforming plant has to be added and for this purpose the oxygen unit has to be larger.

Individual cases will of course have to be evaluated on their own merits, but in general one can say that the co-production and marketing of chemicals from the Fischer–Tropsch plants do make an important contribution to profitability. Moreover, by co-production of the important building blocks, ethylene, propylene, butylene and alcohols and ketones from a coal based process the chemical industry can become less dependent on availability of crude oil products as feedstock.

In summary, co-production of chemicals and motor fuels can be an interesting option for those countries that are not self-supporting in crude oil supplies and have access to coal reserves which can be exploited at reasonable cost.

Discussion

S. P. S. Andrew, F.R.S. (*I.C.I. Agricultural Division, Billingham, U.K.*). Diesel engines are about 1.5 times as efficient as petrol engines. The Fisher–Tropsch synthesis of diesel fuels, however, is much less selective in producing straight-chain paraffins of the diesel fuel molecular mass range than is the Mobil process in producing aromatics in the petrol molecular mass range. May I suggest that what is required is a combination of the two technologies – for instance a Fischer–Tropsch synthesis taking place in a zeolite which would limit the molecular mass of the straight-chain paraffins produced.

J. C. Hoogendoorn. The high efficiency of the diesel engine would indeed stimulate the production of diesel fuel only to get the highest efficiency in terms of 'kilometres per tonne of coal'. The fixed-bed version of the Fischer–Tropsch reaction does indeed produce mainly straight-chain hydrocarbons and by cracking the larger molecules, the fixed-bed system will be able to produce predominantly a wide-range diesel fuel with high cetane numbers, which would be ideal for high-efficiency diesel engines designed to make full use of the qualities of such fuel. Such a wide-range diesel oil will have a flashpoint lower than usual and this will have to be taken into account in the overall design and layout of the diesel vehicle, but this should be no problem, except for special applications such as the use in hazardous areas (underground coal mines, etc.). Even with the present diesel flashpoint specification, it is possible to get a high percentage of the Fischer–Tropsch output in the form of diesel oil of good quality.

An active zeolite, by its very nature, is a very active isomerizing catalyst and so the production of straight-chain paraffins with zeolites does not seem possible.

H. Schulz (*Engler-Bunte-Institut, Universität Karlsruhe, Germany*). In publications and presentations of representatives of the Mobil Corporation it is usually quoted that 'their process' of gasoline production from synthesis gas via methanol is principally superior to the Fischer–Tropsch synthesis in terms of economics, thermal efficiency and product quality. What is Mr Hoogendoorn's opinion about this comparison between the Sasol and the Mobil route, and what arguments did Sasol use for reliance on their process for the next Sasol Three plant?

J. C. Hoogendoorn. A comparison between the Sasol Synthol process and the Mobil process is at this stage rather academic. The Sasol Synthol process is a commercial operation on which exact investment and performance data are available, whereas for the Mobil process such data do not exist. Coal gasification to produce the synthesis gas is the largest part of the investment in both processes and as both processes use the same synthesis gas (2 mol of hydrogen plus 1 mol of carbon monoxide) there is no difference in this step. The Synthol process produces in one step, with a high conversion from the synthesis gas, a mixture of hydrocarbons, which is then further refined into the complete range of liquid fuels (l.p.g., gasoline, jet fuel and diesel oil). In the Mobil process the synthesis gas is first converted to methanol, followed by conversion of methanol to dimethylether and further conversion of dimethylether to hydrocarbons. The hydrocarbons are mainly in the gasoline range and a single product (gasoline) is produced in a relatively simple refinery system. No commercial data exist to judge whether the lower investment in the simpler refinery compensates for the more elaborate three-step conversion of synthesis gas into hydrocarbon molecules. Both processes produce hydrocarbon molecules from an identical synthesis gas, which is a highly exothermic overall reaction. Differences in thermal efficiency between the two processes will therefore be mainly a result of how successful this exothermic heat of reaction can be recovered as useful energy (e.g. high pressure steam). In total, one can say that after commercialization of the Mobil process, it will probably appear that investments and efficiencies of both processes will be of the same order and the choice of process will be dictated by the preference for the product slate.

The decision to build Sasol Three with the Synthol process was the logical result of the sound business philosophy to base an investment of the order of $\$4 \times 10^9$ only on proven technology and on the consideration that when synthetic fuels become a major contribution to the overall transport fuel supply, it is essential that the whole range of transport fuels can be produced, specifically where with fuel conservation, aviation fuel and diesel fuel become more important than gasoline for the overall economic situation of a country.

FIGURE 1. Synthol reactors of Sasol One.

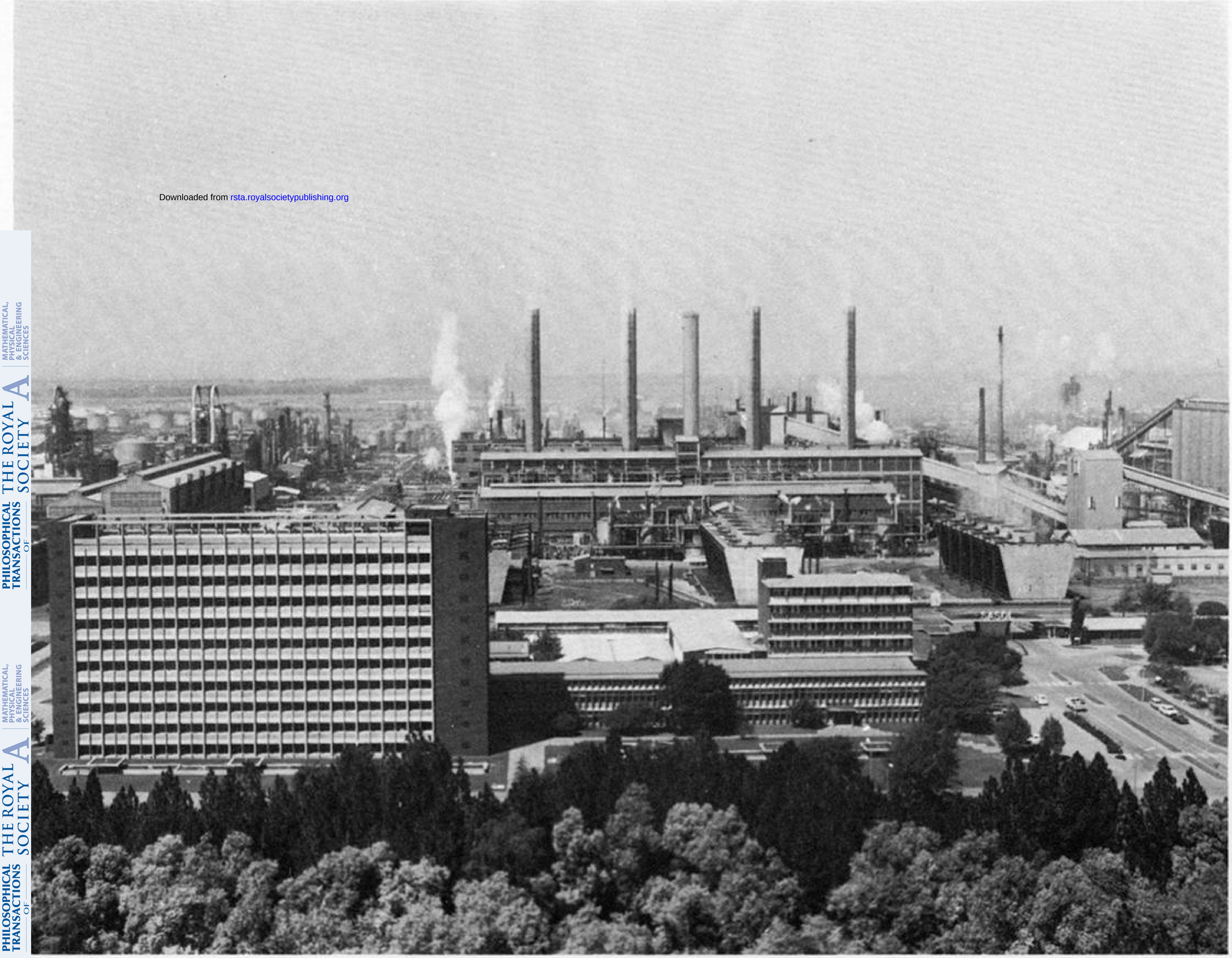

FIGURE 2. General view of Sasol One.

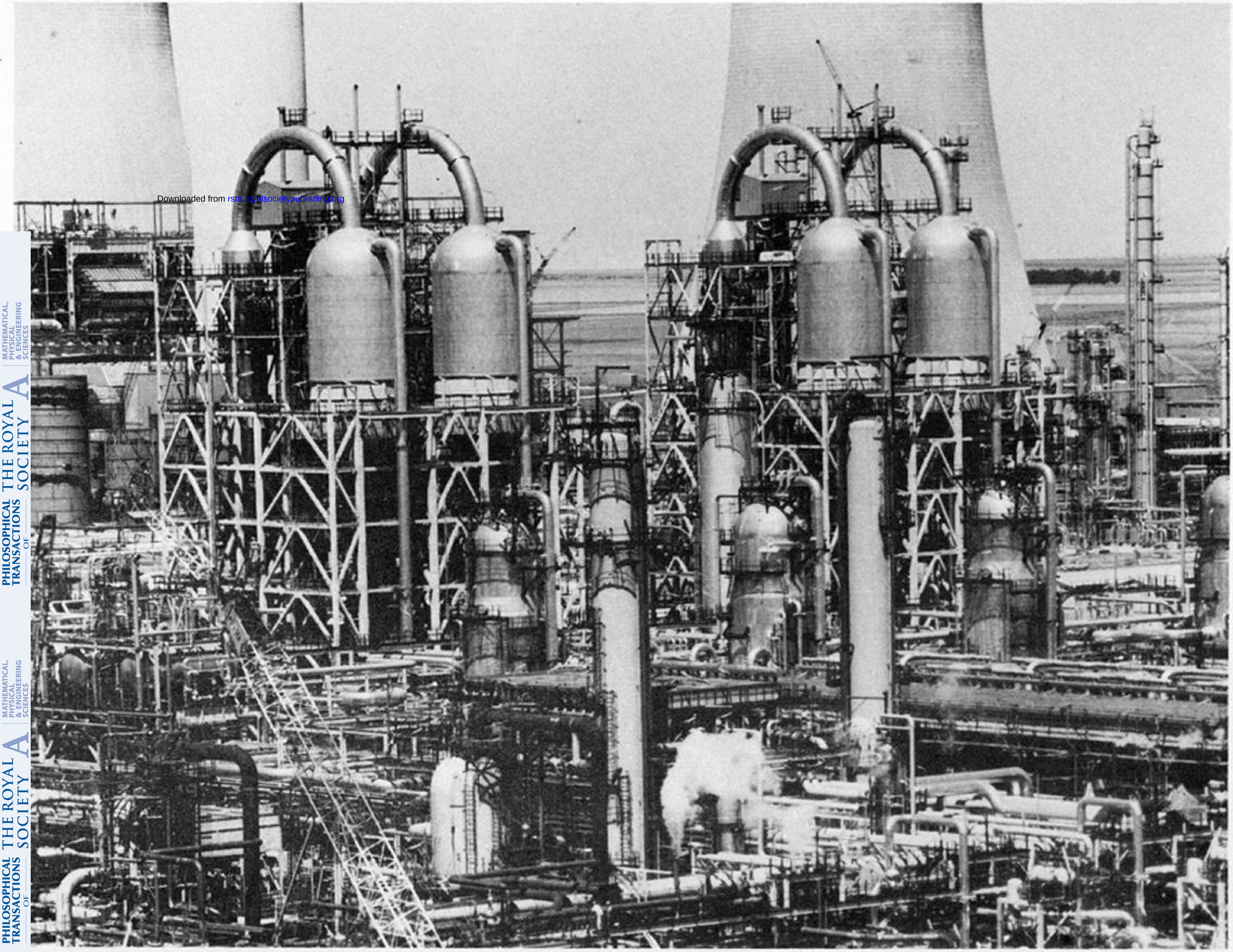

FIGURE 3. Synthol reactor of Sasol Two.

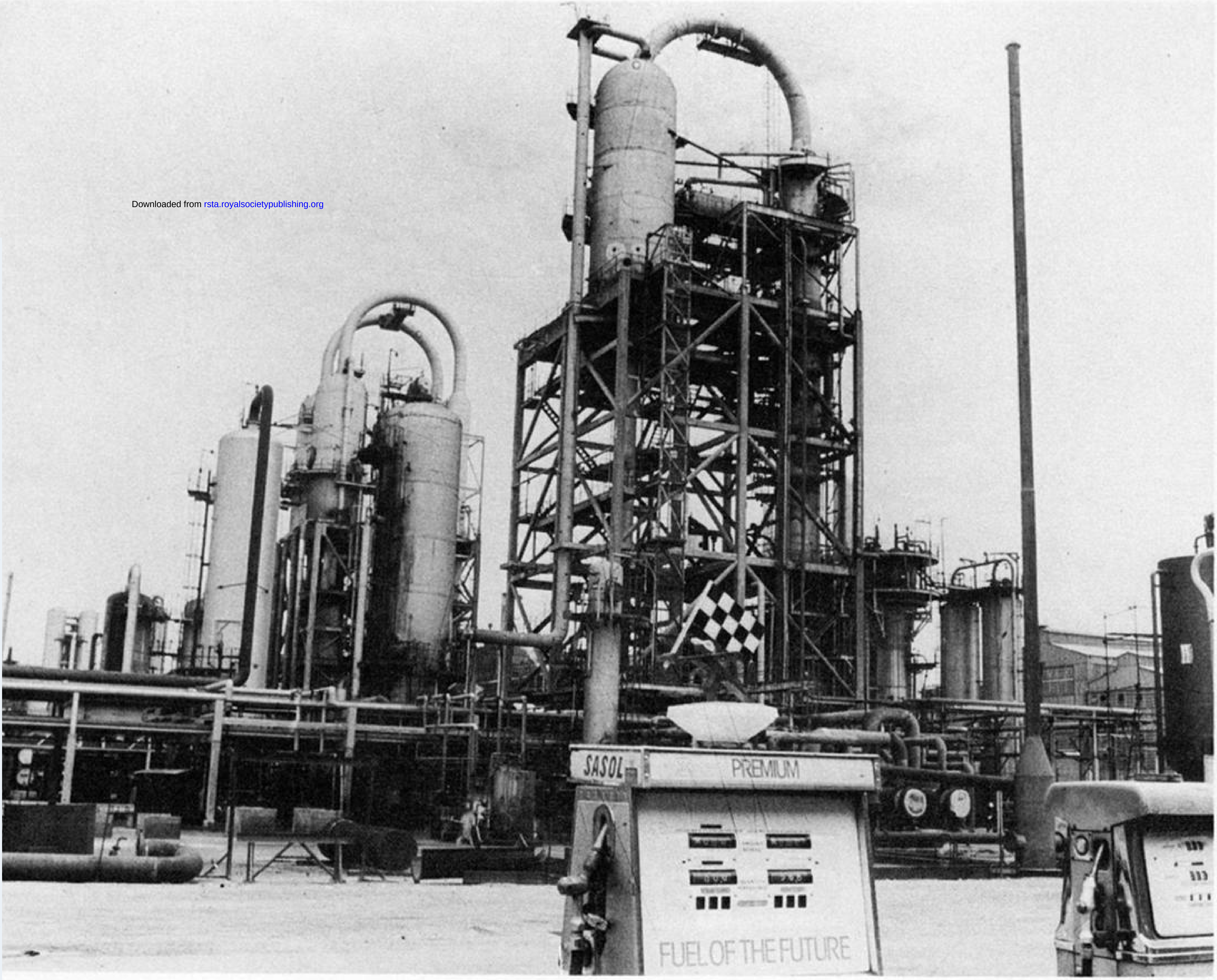

Figure 4. General view of Sasol Two.