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ASSESSMENT OF THE TECHNO-ECONOMIC POTENTIAL OF FISCHER-TROPSCH SLURRY REACTORS,

COUNCIL FOR SCIENTIFIC AND INDUSTRIAL
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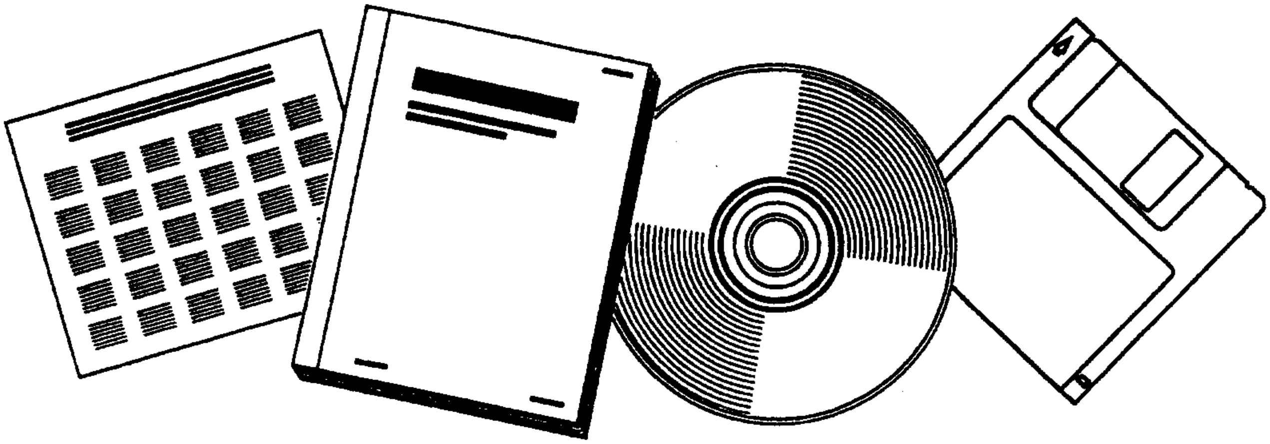

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EVALUERING VAN DIE TEGNO-EKONOMIESE POTENSIAAL VAN FISCHER-TROPSCH FLODDERREAKTORS

D S van Vuuren

Julie 1987

SINOPSIS

Daar is aansienlike ekonomiese potensiaal vir die gebruik van Fischer-Tropsch-flodderreaktors in die Suid-Afrikaanse sintetiese brandstofbedryf, veral in kombinasie met vergassers wat 'n sintesegas produseer met 'n lae waterstofinhoud. Die beraamde koste-voordeel vir hierdie kombinasie in vergelyking met bestaande prosesse is 19 %.

Flodderreaktors maak dit moontlik om sintesegas met 'n lae waterstofinhoud direk te gebruik. Dit verskaf 'n varieerbare produkverspreiding en dit maak hoë omsettings per deurgang moontlik terwyl die voergas stoïgiometries verbruik word. Gevolglik word hersirkulasie tot 'n minimum beperk en die vervaardiging van 'n gasfraksie word grootliks vermy.

Aanbevelings sluit in:

- konsep ontwerpstudies vir vergasser - flodderreaktor kombinasies,
- die ontwikkeling van F-T-flodderreaktortegnologie op 'n loodsskaal,
- die meting van vloeidinamiese ontwerpinligting in F-T-flodderreaktors,
- die ontwikkeling van F-T-katalisators vir gebruik in flodderreaktors, en
- beraming van die vereistes vir die opgradering van die reaktorprodukte.

NATIONAL INSTITUTE FOR CHEMICAL ENGINEERING RESEARCH
COUNCIL FOR SCIENTIFIC AND INDUSTRIAL RESEARCH

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July 1987

SYNOPSIS

Fischer-Tropsch (F-T) slurry reactors have considerable techno-economic potential for the South African synthetic fuels industry, particularly in combination with gasifiers producing a synthesis gas with a low hydrogen content. For this combination, a cost benefit of 19 % compared with existing commercial F-T processes is estimated.

Slurry reactors make it possible to use low-hydrogen synthesis gas, to provide flexibility in the product spectrum and to achieve high conversions per pass with stoichiometric consumption of the feed-gas components. Consequently there is little need for gas recirculation and the generation of a fuel gas fraction can be avoided.

Recommendations cover:

- conceptual design studies of gasifier - slurry reactor combinations,
- development of F-T slurry reactor technology on a pilot scale,
- generation of fluid dynamic design information on F-T slurry reactors,
- development of F-T catalysts for the slurry environment, and
- consideration of the requirements for upgrading the reactor products.

Keywords: gasification, liquefaction, coal, synthesis, liquid fuel, Fischer-Tropsch, slurry reactor, economic potential.

File: 660-50-2

CONTENTS

1 INTRODUCTION

South Africa relies to a large extent on synthetic liquid motor fuels and this reliance is expected to increase in the future. Three SASOL plants are in operation, the Mossel Bay project on liquid fuels from natural gas is in the planning stage and consideration is being given to an AECI coal conversion plant and a Gencor torbanite plant.

The long-term future depends on the discovery by Soekor of oil in exploitable quantities, developments in the international political situation and the introduction of new transport technologies (e.g. ceramic combustion chambers that will allow low-grade fuels to be burnt or large-scale use of electric vehicles). However, due to the abundance of coal reserves throughout the world and especially in South-Africa, coal liquefaction to obtain liquid motor fuels is certainly going to remain an important feature in the field of energy for transport.

The liquefaction of coal can be done either directly, by hydrogenation of high-grade coal with a low ash content, or indirectly via gasification and subsequent hydrogenation of the carbon monoxide in the synthesis gas produced. Synthesis gas may also be produced by reforming of natural gas.

For gasification, a low-grade coal with a high ash content may be used. Due to the availability in South Africa of low-grade coal at relatively low cost and intiatives taken in the development of the gasification-synthesis route, this indirect route has been followed by SASOL.

Two process routes are commercially available for the conversion of synthesis gas to liquid fuels:

- Fischer-Tropsch (F-T) synthesis, and
- a combination of methanol synthesis and methanol conversion.

The latter is used in New Zealand for the production of petrol from natural gas. The F-T process is used at SASOL and will be used at Mossel Bay. The AECI project will probably use the methanol process.

For the F-T synthesis, two reactor types are at present being used commercially:

- the Synthol reactor involving a circulating fluidized bed (CFB reactor) as applied in SASOL 1, 2 and 3, and
- the Arge reactor (fixed-bed reactor), applied at SASOL 1 only.

Alternative reactors for F-T synthesis are:

- the so-called fixed fluidized-bed reactor (FFB), as originally developed by Hydrocarbon Research Inc. in the USA, now being commercialized by SASOL[1], and
- the slurry or Kölbel reactor as originally demonstrated at Rheinpreussen[2] in West Germany.

This report discusses the merits of slurry reactor technology for F-T synthesis in comparison with alternative F-T reactor options.

2 ADVANTAGES AND DISADVANTAGES OF FISCHER-TROPSCH SLURRY REACTORS

2.1 Advantages

- *Low methane-plus-ethane yields*

  Less than 4,6 % compared with 14 % produced in Synthol and FFB reactors (see subsection 3.1.1).
- *Feasibility of using synthesis gas with a low H_2:CO ratio*

  Apart from the Lurgi gasifier, most gasifiers produce synthesis gas with a low H_2:CO ratio that cannot be used directly in the Synthol or FFB reactors (see Annexure 9.1).
- *Flexible product spectrum*

  In contrast to the Synthol or FFB reactors, in which the product spectrum is constrained by the danger of clogging by waxes, the slurry reactor allows an overall diesel-to-gasoline ratio as high as three (that is after oligomerization of the light olefins). A low ratio can be obtained by cracking the heavier products (see Annexure 9.2).
- *Stoichiometric synthesis gas consumption*

  When using synthesis gas with a low H_2:CO ratio, the usage ratio can be matched to the feed ratio, so that little hydrogen remains unreacted (see Annexure 9.3).

- *High single-pass conversion and low recycle*
  Because the usage ratio can be matched to the feed ratio of H_2:CO, little recycling of unreacted synthesis gas is required (see Annexure 9.3).
  High heat transfer rates and simple mechanical construction
  (See Annexure 9.4).

2.2 Disadvantages

Lower space-time yield
Space-time yields similar to those obtained in the Arge and Synthol reactors can be obtained in the slurry reactor when synthesis gas with a low H_2:CO ratio is used. The space-time yield in the FFB reactor is about double that found in the other reactors (see Annexure 9.5).

- *Low-octane petrol*
  Mainly straight-chain hydrocarbons are produced which require upgrading (see Annexure 9.6). However, the products can be fed directly into a fixed-bed reactor for isomerization and aromatization using a ZSM-5-type catalyst, as shown by Kuo[3]. The raw petrol fraction from such a reactor has a research octane number of up to about 95.
- *Separation of catalyst fines from the liquid reactor product*
  This requires additional facilities.
- *Lack of design data and operating experience*
  This has caused the major hold-up in the application of slurry reactors in hydrocarbon processing.

3 ECONOMIC IMPLICATIONS OF SLURRY REACTORS

Although the reactors constitute only a small percentage of the total capital investment in an indirect coal liquefaction process, they form the heart of the whole operation. Changes in reactor type and the concurrent operating characteristics have implications affecting both the upstream and downstream units of the plant. In estimating their economic implications, it is therefore necessary to consider all the operations of a process that will be affected when the reactor is changed, and not only the cost of the reactor unit itself. Detailed economic analyses of this type of effect or of alternative synthetic fuels processes as a whole, have been outside the scope of the activities undertaken to date by the NICER. However, some of the results of such analyses undertaken in the USA for conditions prevailing in the USA have been published and can be used as guidelines.

Shinnar[4] used differential economic analysis to estimate the difference in costs between direct liquefaction (the H-Coal process) and methanol synthesis (without conversion to hydrocarbons). His analysis showed that the difference is not significant. A comparison of direct liquefaction and slurry F-T synthesis, combined with advanced gasifiers, showed that a significant potential saving was possible by using this indirect route. The "best" estimate showed an investment cost of $3100 versus $4100 per million Btu per day of clean product in 1976 values - a potential saving of 25 %.

Table 1 shows the results quoted by Haggin[5] for a UOP comparative study of Synthol, tube-wall, slurry and ebulating bed reactors for the F-T synthesis. Slurry reactors have a clear advantage, but unfortunately the reasons for the differences quoted were not given.

TABLE 1: UOP comparison of Fischer-Tropsch reactors

	Synthol	Tube-wall	Slurry	Ebulating bed
Catalyst ($$10^6$ p.a.)	6,7	14,4	0,7	14,4
Thermal efficiency	66 %	91 %	85 %	85 %
Investment cost index	100	208	46	65

In another study[6] the US Office of Coal Liquefaction Technology worked closely with industry to evaluate SASOL F-T technology and the slurry F-T process combined with advanced gasifier technology.

In terms of 1983 dollars, it was found that the cost of petrol would be $2.48 per (US) gallon for a SASOL F-T plant producing only liquid products and located in Wyoming. If the SNG could be sold rather than reformed, the cost of petrol would be reduced to $2.36 per gallon. With advanced gasifiers and slurry reactors for an all-liquid product plant, the gasoline cost would drop to $1.54 per gallon, a 38 % reduction.

If these figures are converted in a pro rata manner to South African conditions, the potential saving in the capital investment for a fuel plant with the capacity of SASOL 2 would be about one billion Rand p.a. (in 1987 values). For the conversion it was assumed that R1,00 = $0.90 in 1983, SASOL 2 production capacity[7] is 1,4 x 10^6 ton/yr of motor fuels and that an average inflation rate of 15 % prevailed since 1983.

3.1 Estimating the benefits of specific F-T slurry reactor features

The above estimates are probably unrealistic for South African conditions because of different pricing structures. An alternative approach to estimating the benefits is therefore given. These benefits arise from the following major advantages : low methane-plus-ethane yields, ability to use synthesis gas with a low H_2:CO ratio, stoichiometric synthesis gas consumption and high single-pass conversion.

3.1.1 Low methane-plus-ethane yield

Typical product spectra reported for Synthol reactors[7] (also expected for FFB reactors) show methane-plus-ethane yields of 14 %. In the case of slurry reactors, the product spectra can be varied between those reported for Arge reactors and Synthol reactors. A methane-plus-ethane yield of 5 % or less has been demonstrated successfully[2,3,8]. Since four moles of synthesis gas are consumed in the production of methane and only about two moles are regained after steam reforming of methane (see Annexure 9.7), the lower methane-plus-ethane yields of the slurry reactors represent a total increase of 4,5 % in the overall yield of F-T products. A saving in the capital and running costs of the reforming facilities will also result but is not accounted for in this study.

3.1.2 Ability to use synthesis gas with a low H_2:CO ratio

As shown in Annexure 9.1, most of the alternative gasifiers on the market produce synthesis gas with a low H_2:CO ratio. It is also apparent that, of all the gasifiers considered in Annexure 9.1, the Lurgi gasifier produces the most methane-rich synthesis gas. The approximation is made that all gasifiers have equal thermal efficiencies and that only gaseous products are produced, *implying that the cost of separating the phenolic and tar fractions from a Lurgi gasifier and converting them to components for the liquid fuels pool is the same as the cost of converting synthesis gas directly into liquid fuels.*

On this basis a reasonable comparison can be made by calculating the potential amounts of synthesis gas produced by each gasifier per 100 moles of raw gas produced by a Lurgi gasifier. The potential amount of synthesis gas is the sum of the H_2 plus the CO plus two times the moles of methane, since, as shown in Annexure 9.7, steam reforming of methane produces about two moles of synthesis gas per mole of methane reformed. These amounts are given in Table 2.

TABLE 2: Potential synthesis gas production

Gasifier	Total potential synthesis gas	Improvement %
Lurgi	76	-
BGC-Lurgi	79	4,7
Winkler	85	11,8
H.T. Winkler	83,3	9,6
Westinghouse	81,4	7,0
U-Gas	10,5	10,5
Koppers-Totzek	86,4	13,7
Texaco	85,2	12,1
Shell	13,8	13,8
Saarberg-Otto	86,4	13,7

Table 2 shows that improvements in the total amount of synthesis gas of more than 10 % can be obtained in most cases, implying an increase of more than 10 % in the total amount of product from the plant. Note that in the case of the BGC-Lurgi gasifier, the thermal efficiency is much higher[8] than for the Lurgi gasifier (93 % compared with 76 %).

It may be argued that any one of the alternative gasifiers can also be combined with a Synthol or an FFB reactor. This would require changing the composition of the feed-gas to the hydrogen-rich synthesis gas demanded by these reactors. This could be done by placing a shift reactor downstream of the gasifier. However, such a move would result in a loss of thermal efficiency because of a drop in the lower heating value of the gas, which is a good measure of the heat that can in practice be recovered from a fuel[4]. The lower heating value of a synthesis gas with an H_2:CO ratio of two is 255 kJ/mol, compared with 269 kJ/mol for a gas with a ratio of 0,5, the difference being 5 %.

3.1.3 Stoichiometric synthesis gas consumption

As discussed in Annexure 9.3, in the present configuration of Lurgi gasifier and Synthol reactor used by SASOL, an H_2:CO production rate has to be matched with a consumption rate that tends to be lower. This is done by extensive recycling of unreacted hydrogen to suppress the water-gas shift reaction and hence to increase the consumption ratio.

None of the papers in the open literature about SASOL 2 give information about the unreacted hydrogen, but in Annexure 9.3 the following estimate of the overall stoichiometry of the Synthol process is made:

$$CO + 2H_2 \longrightarrow 0{,}871\ CH_{2.3} + 0{,}257\ H_2 + 0{,}742\ H_2O + 0{,}129\ CO_2$$

The analysis shows that 0,26 moles of H_2 per mole of CO fed to the reactors remain unconverted. Since this represents 8,6 % of the total synthesis gas produced, a potential increase of 8,6 % in total liquid motor fuels could be achieved by a process in which the H_2:CO usage ratio matches the supply ratio exactly. Such an increase can be brought about by combining advanced gasifiers and slurry reactors. In financial terms, this means about a 4 % increase in income because the gas can be sold at about half the price of petrol (see Annexure 9.8).

3.1.4 High single-pass conversion and low recycle

As discussed in Annexure 9.3, when the slurry reactor is combined with alternative gasifiers producing synthesis gas with a low H_2:CO ratio, it can operate with virtually no recycling, compared with the recycled-to-fresh-feed ratio of two used for the Synthol reactors. A considerable saving can therefore be made by decreasing the sizes of downstream condensers, heat exchangers and compressors. However, as pointed out in Annexure 9.4, the reactor size will have to be more or less twice that of an FFB reactor and the petrol fraction will have to be upgraded more extensively. For the purpose of this analysis it is assumed that these effects balance out.

3.1.5 Summary of the potential savings related to slurry reactors

The potential savings pointed out in the above analyses add up to a potential increase in income of about 19 % if slurry reactors combined with alternative gasifiers are used. For a plant producing 1,4 x 10^6 tons of motor fuels per annum (the SASOL 2 design production figure[7]) at a cost of about R0,50 /litre, *this works out at a saving of R 190 x* 10^6 *per year.*

of our lower coal prices, potential gasifier sales for them and the lower salaries of South African professionals. Consideration should be given to forming a team made up of experts from various interested parties in South Africa, including the National Institute for Coal Research of the CSIR, to carry out a comparative non-experimental evaluation of gasifiers.

6. CONCLUSION

The application of Fischer-Tropsch slurry reactors has considerable economic potential for the South-African synthetic fuels industry, particularly in combination with alternative gasifiers.

7. RECOMMENDATIONS

7.1 Conceptual design studies of gasifier - slurry reactor combinations

Realistic conceptual plant studies applicable to South African circumstances would quantify the economic potential of alternative gasifiers combined with F-T slurry reactors more precisely. This should preferably be done by an industrial concern with the necessary experience. The NICER could provide assistance with the task.

7.2 Pilot-scale development of F-T slurry reactor technology

This work should deal in particular with the use of low H_2:CO ratios in the synthesis gas, in order to determine the ratio having the greatest economic potential. Pilot-scale work is feasible only in industry. The NICER could act in an advisory capacity.

7.3 Generation of fluid dynamic design information on F-T slurry reactors

Knowledge of the fluid dynamic behaviour inside the reactor is as important as knowledge of the catalyst when scaling up the reactors. Continuation of the research on this subject at the NICER is recommended. In addition, the techniques already developed should be applied to take measurements in the proposed pilot-scale unit, in cooperation with the industry operating this unit.

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7.4 Development of F-T catalysts for the slurry environment

The F-T catalyst used in the fixed-bed Arge reactors, in which it is well-wetted by wax formed during the synthesis reaction, is not necessarily the best catalyst for use in slurry reactors. The development of F-T catalysts specifically for slurry reactors is therefore recommended, together with their evaluation under various operating conditions. Both SASOL and the NICER have expertise and facilities to undertake such development; a joint programme could be considered.

7.5 Upgrading of products

Consideration should be given to the requirements for upgrading the F-T slurry reactor products to liquid fuels. The industrial concern responsible for the pilot-scale demonstration should lead the task of upgrading the products. NICER and researchers at universities such as the Witwatersrand, Cape Town and Potchefstroom can also provide assistance.

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9 ANNEXURES

9.1 H_2:CO ratio and alternative gasifiers

The overall economics of coal liquefaction are greatly influenced by the cost of producing synthesis gas. For example, Kölbel and Ralek[2] claimed that the cost of synthesis gas amounts to more than 80 % of the overall costs. Dry[17] attributed 58 % of the running costs in a typical F-T plant to synthesis gas production (95 % of the 58 % being for coal gasification). The difference in the figures quoted by Kölbel and Dry is most probably due to the fact that Kölbel's figure includes the cost of mining and that these figures relate to different countries with different conditions.

However, from these figures it is clear that gasification is the most costly operation in the overall liquefaction process. Gasification is equally important in the methanol conversion route for liquefying coal because methanol is also made from synthesis gas. Any saving in the gasification cost will therefore have a significant effect impact on the overall process economics of both the F-T and the methanol conversion processes.

The so-called second-generation gasifiers potentially have considerable economic advantage over the traditional gasifiers, but in general synthesis gas of low H_2:CO ratios is produced. Table 3 compares the compositions of the gas produced by various alternative gasifiers[19].

The Lurgi, Koppers-Totzek and Winkler gasifiers have been proved extensively on a commercial scale[18], and the other gasifiers are in an advanced stage of development or demonstration. Apart from the Lurgi gasifier, all the gasifiers produce a gas with an H_2:CO ratio well below 2 and in most cases below 0,7.

Such low-hydrogen synthesis gas cannot be treated directly in a Synthol or an FFB reactor due to excessive carbon formation at high temperature. Slurry and Arge reactors, on the other hand, can process these CO-rich gases directly.

Table 3 COMPOSITION OF GAS FROM GASIFIERS

Gasifier	Coal type	% vol. (dry)				H_2:CO
		H_2	CO	CO_2	CH_4	
Lurgi	bituminous	40	18	30	9	2,22
BGC-Lurgi	bituminous	28	61	3	6	0,46
Winkler	lignite	41	36	20	2	1,14
H.T. Winkler	lignite	35	52	9	3	0,67
Westinghouse	bituminous	32	51	10	5	0,63
U-Gas	bituminous	45	36	16	2	1,25
Koppers-Totzek	bituminous	32	55	11	-	0,58
Texaco	bituminous	38	46	12	1	0,83
Shell	bituminous	29	64	4	-	0,45
Saarberg-Otto	sub-bitumin.	29	61	7	-	0,48

9.2 Flexible product spectrum

In general the F-T process is fairly unselective in that it always produces a spectrum of products rather than one specific product. This spectrum of products can be shifted towards either lighter or heavier products by changing the catalysts or operating conditions. The distribution of products is usually described reasonably well by the so-called Schulz-Flory distribution[19].

In the case of the Synthol and FFB reactors, the product spectrum must be kept on the light side (by operation at a relatively high temperature), because an excess of condensed heavier products will cause catalyst agglomeration and subsequent deterioration of the fluidized catalyst bed. The operating conditions are responsible for the large amount of methane and ethane produced, as mentioned before. This does not apply to the slurry or Arge reactor types in which process conditions can be varied to a greater extent in order to provide a basic feedstock that is more suitable for upgrading to fuels that meet the market demands.

Variability in the product slate for slurry reactors was illustrated by Kölbel and Ralek[2] with numerous examples whereas Dry[20] showed that for the Synthol reactor up to 55 % of the reactor product ending up in the liquid fuels pool may be diesel. For the Arge-type reactor, diesel yields of up to 75 % of the total liquids can be achieved by upgrading, including wax cracking. The yield of liquid products (after upgrading) is 77 % of the total hydrocarbon products in the case of the Synthol reactor, compared with 87 % for the Arge reactor.

9.3 Stoichiometric synthesis gas consumption and low recycle

In the F-T process, two reactions are of prime importance: the F-T and the watergas shift reactions. These reactions are given by equations (1) and (2) respectively. The H:C mol ratio in the hydrocarbon product is close to 2 because most of the methane is reformed and the olefin content of the product is high.

$$2H_2 + CO \longrightarrow -CH_2- + H_2O \qquad (1)$$

$$H_2O + CO \rightleftharpoons CO_2 + H_2 \qquad (2)$$

Depending on the extent of the watergas shift reaction, the ratio of H_2:CO consumption can vary between 0,5 and 2,0, whereas the supply ratio from the Lurgi gasifiers is about 2,0. If the consumption ratio is lower than the feed ratio, some of the synthesis gas is not utilized. This unutilized fraction must be used or sold as fuel gas, which does not have a high value in South Africa.

Detailed mass balances of the SASOL plants are not available in the open literature to show the extent to which this problem is experienced at SASOL. In fact the existence of a gas product stream at SASOL 2 is shown on the flowsheets given in only two references[21,22]. However, a reasonable estimate can be made from a collection of bits of published information.

Firstly, it is known that at high temperatures the watergas shift reaction approaches equilibrium in F-T reactors[23]. The equilibrium constant has a value of about 26 at the Synthol reactor temperature. The ratio of carbon dioxide to water can therefore be calculated from equation (3), if the H_2 and CO concentrations in the exit gases from the reactors are known.

$$[CO_2]/[H_2O] = K_w[CO]/[H_2] \qquad (3)$$

Furthermore it is known that the fresh gas H_2:CO ratio in the SASOL 2 plant[22] is 2,0 and that the ratio of recycled to fresh feed[24] is also about 2,0. Assuming that the average H:C ratio of the product formed in the overall synthesis (after oligomerization and hydrogenation) is 2,3 (the ratio for octane is 2,25), and that the single-pass CO conversion is 96 % (the conversion claimed for the Hydrocol FFB reactor[1]), it can be shown (see Fig. 1) that the overall stoichiometry, when all the unconverted CO is recycled, is as follows:

$$CO + 2H_2 \longrightarrow 0{,}871\ CH_{2,3} + 0{,}257\ H_2 + 0{,}742\ H_2O + 0{,}129\ CO_2 \quad (4)$$

The amount of CO recycled per mole of CO fed to the reactors is 0,04 moles and the $CO + CO_2$ conversion is 87 %, which agrees reasonably well with the value of 85 % which Dry[1] claimed can reliably be achieved in the Synthol reactor.

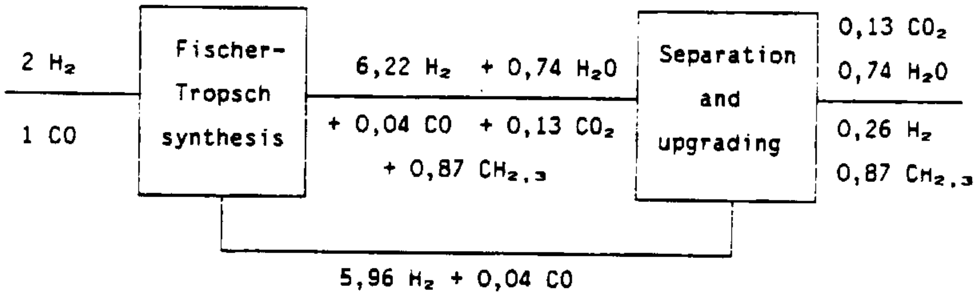

Fig. 1 Overall stoichiometry of the F-T synthesis complex

This analysis is rather sensitive to the assumptions of single-pass CO conversion and recycling. For example, if a single-pass CO conversion of 98 % is assumed, a loss of unreacted hydrogen of only 2,8 % results. However, the $CO + CO_2$ conversion per pass increases to 93 % (in contrast to the claim of 85 %) and the H_2:CO ratio in the exit gas increases from 149 to 297. Such an increase in the H_2:CO ratio in the synthesis gas is bound to have an adverse effect, because it increases the formation of methane and decreases the olefinicity of the light hydrocarbon products.

The economically optimum condition is not known to the author because of its proprietary nature. In the case of an increased recycle of 2,5, it follows that the synthesis gas "lost" in the form of unreacted H_2 drops to 6,6 % and the H_2:CO ratio in the exit synthesis gas increases to 183.

When a slurry reactor is used in combination with alternative gasifiers producing a synthesis gas with a low H_2:CO ratio, virtually no recycle (a recycle ratio of about 0,1) is required. The reason for this is that the watergas shift equilibrium constant is high and that iron-based catalysts normally have a high watergas shift activity. Therefore, most of the water produced by the Fischer-Tropsch reaction reacts with carbon monoxide to produce more hydrogen. The nett result is that better agreement between the usage and supply ratios of the H_2 and CO is obtained without the requirement of large recycle ratios. Recycle is merely used to reprocess about 10 % unreacted synthesis gas. The cost associated with "lost" synthesis gas as well as the cost of downstream condensers, heat exchangers and compressors is therefore reduced.

9.4 Simple mechanical construction

Heat removal is specifically problematic in the Arge reactor. This is the reason for a complex reactor construction (2 052 reactor tubes of 0,046 m in diameter, in a shell with a 3 meter diameter[24]) and the use of high gas flow rates (high recycle) to enhance the heat transfer. Because of the cooling by steam generation in the shell, the shell construction must be able to withstand steam at 523 K and 4 000 kPa, although the reactor tubes operate only at 2 300 to 2 500 kPa. The fact that the shell is already designed to withstand higher pressures than are normally used in the reaction tubes makes it an attractive proposition to operate existing Arge reactors as "high-pressure Arge" reactors. Higher space-time yields can be expected, but also more temperature-control problems.

Synthol, FFB and slurry reactors have excellent heat transfer characteristics due to the large circulation currents of the fluids in these reactor types. The scaling up of the diameters of these reactor types is therefore not limited by heat transfer restrictions. The result is that the FFB and slurry reactors have simple mechanical constructions. The construction of the Synthol reactor is complex because of the catalyst circulation and catalyst-gas separation techniques.

9.5 Space-time yield

The space-time yield of the different reactor types increases in the order: slurry, fixed-bed, Synthol, FFB. Koppers[25] of Rheinpreussen claimed slurry reactor space-time yields of up to 2 800 kg/m^3 in a laboratory reactor, but in all the other studies published by his group considerably lower values were reported (e.g. 940 kg/m^3 per day in a pilot-scale reactor and 740 kg/m^3 per day in a laboratory reactor). These lower values were ascribed to the reactor pressure being low due to insufficient compression facilities, i.e. only 1 200 kPa instead of about 2 500kPa at which pressure F-T reactors are still expected to work satisfactorily. Because space-time yield is a relatively linear function of pressure, it is reasonable to assume that space-time yields of up to 2 000 kg/m^3 per day are attainable in slurry reactors, based on the reported Rheinpreussen results.

It is a matter for concern, however, that even the lower reported space-time yields could not be reached by other researchers. Hall *et al.*[10] found about 475 kg/m^3 per day, Mitra and Roy[13] reported 585 kg/m^3 per day and Schlesinger *et al.*[12] about 382 kg/m^3 per day. It is only fairly recently that Gaube[26] and Deckwer and Sanders[27] have reported results with catalyst activities high enough to match the results reported for the Rheinpreussen demonstration plant.

In contrast with the slurry reactors, fixed-bed reactor space-time yields exceeding 1 000 kg/m^3 per day have been reported by several investigators. Hall *et al.*[10] found a yield of C_2^+ products of 1 312 kg/m^3 per day in a fixed-bed reactor and the reported SASOL Arge reactor space-time yield[24] is about 1 250 kg/m^3 per day.

Space-time yields for the Synthol reactor cannot readily be calculated from the results reported in the literature because the exact dimensions of the Synthol reactors are never fully disclosed. Deckwer[24] reported the following information on the SASOL 1 Synthol reactor : reactor height 36 m, reactor diameter 2,2 m, catalyst settling-hopper diameter 5 m, 60 000 tons of products per year and about 80 % time on stream. Assuming that the heights of the reaction zone and the hopper are only a quarter of the total height of the construction, a space-time yield of only 700 kg/m^3 per day is obtained.

For the SASOL 2 Synthol units, the following information has been published[23]: reactor structures 75 m high, reactor diameters of 3 m and design capacities of 300 000 to 350 000 m^3/h. Assuming 100 % conversion at the higher capacity, C_3^+ yields of 0,16 kg/m^3 synthesis gas converted, 80 % time on stream, reactor and hopper heights of a quarter of the total structure height and a catalyst settling-hopper diameter of 6,8 m (the same ratio between the cross-sectional areas of the reactor and catalyst hopper as for the SASOL 1 Synthol reactors), a space-time yield of C_3^+ products of 2 065 kg/m^3 per day is implied by the results.

Kölbel and Ackermann[28] referred to space-time yields of between 4 000 and 12 000 kg/m^3 per day for the Hydrocol process, but also claimed that the highest demonstrated yield was only 5 000 kg/m^3 per day. Dry[1] referred to results obtained in the FFB reactor obtained by Hydrocarbon Research Inc. in which 96 % conversions were obtained at fresh feed space velocities between 2 000 and 3 000 per hour. Assuming a C_3^+ yield of 0,16 kg/m^3 of synthesis gas converted, this claim implies a space-time yield of 9 200 kg/m^3 per day. In contrast with this high yield, the design specifications of the plant suggest a much lower space-time yield. The design capacity of 360 000 tons/yr per reactor, with dimensions of 5 m in diameter by 18 m in height, imply a space-time yield of 3 840 kg/m^3 per day at 80 % time on stream. The difference between these calculated space-time yields arose because the space velocity was based on the expanded catalyst-bed volume and not on the total reactor volume[29].

From this discussion it is clear that comparison of the space-time yields of the various reactor types is ambiguous. However, by considering the characteristics of the slurry and FFB reactor types, an approximation of the maximum ratios of space-time yields is derived below.

From Kölbel's and Ralek's results[2], it appears that a superficial gas velocity of 0,1 m/s is more or less optimum for the slurry reactor because greater gas velocities will cause the formation of large bubbles which will effectively bypass the reacting slurry. It is futhermore apparent that increased catalyst activity will also have little effect on the space-time yield since the conversion was already about 90 %.

In contrast with the above "optimum" velocity and hence space-time yield for the slurry reactor, FFB reactors are limited by a maximum gas velocity. This maximum gas velocity is determined by the extent to which the loss of fine catalyst particles can be tolerated. The rate at which these fine particles are formed is a function of the attrition resistance of the particles loaded into the reactor. The attrition resistance, on the other hand, is a function of the synthesis gas composition, because excessive carbon formation weakens the mechanical strength of the particles. All these effects preclude a simple calculation of the maximum velocity, but a reasonable estimate can be made from published information.

The maximum throughput of the Synthol reactor is determined by a similar catalyst-entrainment criterium in the catalyst settling hopper. From the information given by Deckwer[24] for the SASOL 1 Synthol reactor (temperature of 623 K, pressure of 2 000 kPa, fresh feed flow rate of 100 000 Nm^3/h, recycle ratios of up to 2,5 and a reactor diameter of 5 m), it follows that the gas velocity in the hopper is about 0,52 m/s. From operating data of the Hydrocol FFB reactor (temperature of 593 K, pressure of 2 700 kPa, recycle-plus-fresh-feed rate for two reactors[29] of $1,2 \times 10^6$ Nm^3/h and a reactor diameter of 5 m), it follows that the linear gas velocity in the reactors was 0,62 m/s. Provision was made for subsequent gas-solid separation in order to return entrained catalyst to the reactors. Lastly, in bench-scale studies reported by Dry[1], linear gas velocities of up to 0,45 m/s were used. These considerations strongly suggest that for the catalysts used by SASOL, the limiting linear gas velocity in an FFB reactor is about 0,6 m/s.

Due to the requirement of a high hydrogen concentration in order to reduce carbon formation and to have H_2:CO usage ratios similar to that supplied by the Lurgi gasifiers, a recycle ratio above 2 is normally used. This reduces the effective velocity of the fresh feed gas to 0,2 m/s. As is the case with slurry reactors, increased catalyst activities have little effect on this maximum velocity and hence on the space-time yield; they can only save on the cost of the catalyst itself.

Assuming that the reactor lengths used for commercial-size slurry and FFB reactors are the same (which is a conservative assumption because an 8,6 m high slurry reactor was used in the Rheinpreussen[2] demonstration plant and an 18 m FFB reactor in the Hydrocol plant[1]), the ratio of the products of the maximum fresh feed velocities and the maximum conversions is equal to the ratio of the space-time yields. In the cases of a second-generation gasifier coupled to a slurry reactor versus a second-generation gasifier coupled to an FFB reactor, or versus a Lurgi gasifier coupled to an FFB reactor, it follows that the space-time yield of a slurry reactor is about a half that of an FFB reactor. In the case of a Lurgi gasifier with a slurry reactor, a large recycle has to be used as well for stoichiometric reasons. However, a lower recycle than for an FFB reactor can presumably be used because at the lower temperatures at which slurry reactors operate, the watergas shift activity is lower, so that a recycle ratio of 1 instead of 2 seems reasonable. This gives a fresh feed velocity of about 0,05 m/s, so that the space-time yield can be expected to be about four times lower than in an FFB reactor.

9.6 Petrol with a low octane rating

The F-T process has the inherent characteristic of producing mostly linear hydrocarbons. This is excellent feedstock for diesel production but poor for petrol, in which highly branched and aromatic components are desirable to raise the octane number. However, in the high-temperature F-T processes (Synthol and FFB), sufficient branching and aromatization occur to influence the octane number of the straight-run feedstock. Dry[30] reported 65 % olefins, 14 % paraffins, 7 % aromatics, 6 % alcohols, 6 % ketones and 2 % acids in the petrol fraction produced in the Synthol reactor. Only 55 % of the paraffin fraction is n-paraffins. This results in a research octane number of 88 compared with a reasearch octane number of about 35 for the straight-run gasoline fraction produced by the Arge reactor.

The slurry reactor yields a more olefinic product than the Arge reactor, but very few aromatics are produced. Because the products are mainly straight-chain hydrocarbons, a low octane number can be expected. Unfortunately no value has been reported in the literature. However, the high olefinicity of the product allows easier upgrading of the products, as demonstrated in the Mobil two-stage F-T ZSM-5 process. For this process Kuo[3] reported octane numbers of the straight-run gasoline product as high as 95. In the two-stage process, the gaseous effluent from the Fischer-Tropsch slurry reactor is fed directly to a fixed-bed ZSM-5 reactor for isomerization and aromatization. Although this process appears to give a raw product superior to that from the Synthol reactor, it must be realized that an extra reactor type is included in the process.

9.7 Methane reforming

In considering the synthesis of methane, it should be noted that four molecules of synthesis gas are required to produce one molecule of methane according to:

$$3\ H_2 + CO \longrightarrow CH_4 + H_2O \qquad (5)$$

After synthesis, the methane is cooled down in order to separate it from the unreacted synthesis gas and other products, and it is then converted back into synthesis gas by the steam-reforming reaction. This reaction is endothermic so that part of the methane must be oxidized in order to provide the heat of reaction. At SASOL 2, Lurgi auto-thermal, catalytic, partial-oxidation reformers are used[22]. For an ideal process producing a synthesis gas with an exit H_2:CO ratio of 3, the stoichiometry is approximately as follows:

$$CH_4 + 0{,}342\ H_2O + 0{,}439\ O_2 = 0{,}781\ CO + 2{,}342\ H_2 + 0{,}219\ CO_2 \qquad (6)$$

This implies that for every mole of methane converted only 3,123 moles of synthesis gas are produced. Real steam-reforming processes operate[31] at efficiencies of about 70 %, so that in a real process about 0,7 x 3,123 = 2,19 moles of synthesis gas are produced. This is about half of the synthesis gas consumed originally to produce the methane. (This estimate of the loss of synthesis gas is confirmed by the mass balances over the reforming units reported by Dry[7]). An increase in total liquid fuels equal to half the total amount of methane produced in the Synthol reactors can therefore be attained by using a process that produces no methane at all.

9.8 Gas and petrol prices

In the South African context it is more advantageous to produce liquid fuels instead of gas from coal because there is no infrastructure for consuming large volumes of gas. This is reflected to some extent by the prices of gas relative to those of petrol in the Transvaal and in the Cape. In the Cape Peninsula the price[32] of regular petrol (excluding taxes and duties) was 35,2 c/litre in December 1986, whereas the price of gas for commercial use varied between R 24,72 and R 29,47/GJ[3]. In the Transvaal the gas price varied between R 5,41 and R 9,69/GJ, whereas the estimated price for regular petrol was 40 c/litre (only the pump prices are cited in reference 3). By converting the price of petrol from a per-litre basis to a per-gigajoule basis, it follows that the equivalent energy price for petrol was about R 10,60/GJ in the Cape and about R 12,00/GJ in the Transvaal.

The reason for the price of gas being more than twice that of petrol in the Cape is that the gas is derived from crude oil. This is not in abundant supply and the market is small. In the Transvaal however, the price of gas can in some cases be as low as about half the price of petrol. This is presumably so because a large amount of gas is produced by SASOL. The low price is an incentive to increase the market.

9.9 Summary of F-T slurry reactor research

After Kölbel's pioneering work in Germany to develop the Rheinpreussen slurry reactor process after World War II, active research was also begun in Britain at the DSIR Warren Spring Laboratories[10,11] and in the USA at the US Bureau of Mines[12,13]. Research was subsequently also undertaken in Japan[2] and in India[14]. The results obtained by Kölbel were very favourable, but none of the other groups seemed to be able to obtain similar space-time yields or catalyst activities.

All this early development work was stopped in the late Fifties and early Sixties because of the increasing availability of crude oil. It was only in the late Seventies that the oil crises sparked off renewed interest in synthetic fuel production.

The main groups undertaking slurry reactor research in the second era are those of Prof. W-D Deckwer at the University of Oldenburg, West Germany, Prof. J Gaube at the University of Darmstadt, West Germany, Prof. C N Satterfield at MIT in Boston, USA, Prof. A T Bell at Berkeley, USA, and Air Products and MOBIL, both in the USA. In South Africa research has been undertaken at the Universities of Pretoria and Potchefstroom, at the NICER - CSIR and at SASOL.

Deckwer initially concentrated on the fluid-dynamic properties of bench-scale slurry reactors but later continued by measuring the intrinsic kinetics of the F-T reaction. His group pointed out that the F-T process is kinetically controlled in the slurry phase and they also managed to achieve catalyst activities high enough to match Kölbel's results.

The purpose of Gaube's work was to produce linear olefins via the Fischer-Tropsch synthesis. Fixed-bed and slurry reactors were used to determine the kinetics of primary reactions as well as of the secondary isomerization and hydrogenation reactions. The effects of catalyst compositions and operating conditions were studied in detail. The activities found by Gaube matched that of the catalyst used in the Rheinpreussen slurry reactor.

Satterfield concentrated on studying mass transfer and kinetics in a well-mixed slurry reactor using an ammonia synthesis catalyst (a good standard for comparing against other results). Extensive analysis of the products revealed that the product spectrum should be described by a superposition of two Schulz-Flory distributions and not by only one as was accepted by many.

Bell's group also measured kinetics and mass transfer rates in a well-mixed slurry reactor, but in addition provided the most extensive mathematical model for the design of slurry reactors. The model takes into account the kinetics of the F-T as well as the watergas shift reaction, interfacial mass transfer rates, stoichiometry, and gas and liquid phase backmixing.

Air Products started with the measurement of pilot-scale fluid dynamics and heat transfer rates, and with catalyst development. Apparently this work was later subcontracted to Prof. Bukur at the Texas A&M University.

The most extensive work to date (apart from the work at Rheinpreussen) has been undertaken by MOBIL. A two-stage F-T slurry ZSM-5 process was developed and extensively demonstrated on a pilot scale. Extensive analysis of the products from both the slurry and ZSM-5 reactors was undertaken, the fuel quality was measured, techniques for upgrading the products were established and long-term runs were performed to prove stability (up to three months continuous running of a bench-scale plant). In addition, fluid dynamics were measured in hot-flow bubble columns and conceptual design studies were performed.

Locally some kinetic studies have been undertaken at the University of Pretoria but these have been discontinued. At the University of Potchefstroom the kinetics of the Fischer-Tropsch reaction were studied using a ruthenium catalyst in a slurry reactor. This work has also been discontinued.

At the NICER a programme was started to measure fluid-dynamic properties in a pilot-scale slurry F-T system. Various experimental techniques have been developed to measure bubble sizes, gas hold-up, backmixing, and the solubility and diffusion of the various components in the wax medium. This work is still in progress and is at present being complemented by kinetic measurements in a well-mixed slurry reactor.

SASOL is also studying the slurry F-T reactor on a bench scale, specifically geared to conditions at SASOL, where Lurgi gasifiers are used. Only limited results have been published in the open literature because of the proprietary nature of SASOL's operations.