SYNTHETIC FUELS FROM ATMOSPHERIC CARBON DIOXIDE

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I  Introduction

The predicted shortages of fossil fuels at some indefinite time in the future naturally gives rise to a search for alternatives. Shall we or our successors ultimately be dependent on electric power used directly or stored in electrochemical batteries? Alternatively, will there still be a role for energy stored and distributed in the form of liquid fuels? Also one wishes to know the most probable source of these synthetic fuels. Will it be best to use coal and tar sands as the source of energy or will nuclear power be more attractive?

In assessing the most probable routes which future energy distribution will take, operating and capital costs are of critical importance. Yet in dealing with the cost of a process which is not yet practised it is very difficult to be very precise in one's estimates. Nevertheless, in this paper an attempt is made to suggest the orders of magnitude of cost involved in making synthetic fuels derived essentially from carbon dioxide and water with the addition of energy from a non-fossil source. It is assumed that such a course might be desirable at some time in the future when fossil fuels are relatively scarce and nuclear power comparatively inexpensive.

For automotive use the convenience of a liquid fuel is very desirable and the most conveniently produced liquid fuel, given supplies of carbon dioxide and water, is methanol. Hydrogen may be produced by electrolysis of water and with the addition of carbon dioxide by a suitable catalytic process, methanol results:

Overall reactions: $3H_2 + CO_2 \longrightarrow CH_3 OH + H_2O$
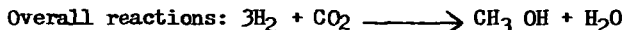
Alternatively, it would be possible to make hydrocarbons by the Fischer-Tropsch reaction.

Thus, given the costs of making hydrogen and obtaining carbon dioxide and adding the cost of a synthetic process involved, it is possible to gain some idea of the cost of either methanol or a synthetic hydrocarbon fuel. It should be emphasised that the costs (calculated on a 1970 basis of money values) are based on figures obtained from various references and are not plant costings made by the appropriate Divisions of the Royal Dutch/Shell Group of companies.

In this paper the cost of hydrogen manufacture will be first considered followed by the cost of obtaining carbon dioxide. The synthetic processes for methanol production and Fischer-Tropsch hydrocarbon synthesis then follow.
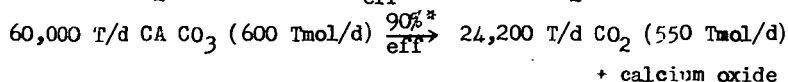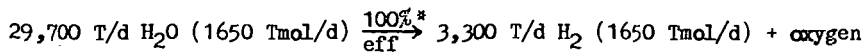
Rough estimates are made of the capital employed, the energy consumed and manufacturing costs on a stated basis. In order to put the synthetic fuel route into perspective, a comparison is made with the costs of coal based fuels. Also the overall efficiency achieved by using fuels in gasoline engines and fuel cells is compared with electricity stored in batteries and used to drive electric vehicles.

II  Processes and economics to manufacture "non fossil" methanol
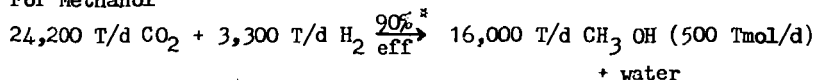    and Fischer-Tropsch gasoline

1. Scale of operation and overall reactions

A relatively large plant has been chosen since it is assumed that the fuel would be required for the domestic market: a methanol production of 16,000 Tonnes per day (T/d) or alternatively 9,000 T/d Fischer-Tropsch gasoline. The lower heating values (LHV) of those products is $26.10^9$ Tcal/year; and is equivalent in LHV with $2.8\ 10^6$ T/a automotive fuel, the output of a typical modern refinery.
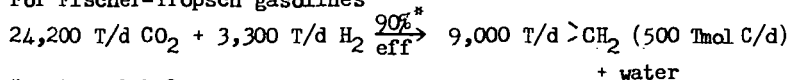
The overall reactions of the processes which will be discussed in the next section are:

29,700 T/d $H_2O$ (1650 Tmol/d) $\xrightarrow[\text{eff}]{100\%\,*}$ 3,300 T/d $H_2$ (1650 Tmol/d) + oxygen

60,000 T/d CA $CO_3$ (600 Tmol/d) $\xrightarrow[\text{eff}]{90\%\,*}$ 24,200 T/d $CO_2$ (550 Tmol/d)

$+$ calcium oxide

For Methanol

24,200 T/d $CO_2$ + 3,300 T/d $H_2$ $\xrightarrow[\text{eff}]{90\%\,*}$ 16,000 T/d $CH_3$ OH (500 Tmol/d)

$+$ water

For Fischer-Tropsch gasolines

24,200 T/d $CO_2$ + 3,300 T/d $H_2$ $\xrightarrow[\text{eff}]{90\%\,*}$ 9,000 T/d $>CH_2$ (500 Tmol C/d)

$+$ water

\* material balance efficiency

2. Description of Processes

(a) Hydrogen Production

If fossil fuels are ruled out as a source of hydrogen then hydrogen by high pressure electrolysis of water is the obvious route. This subject has been considered in detail by Costa and Grimes[1] and data derived from their work are given in Table 1 which summarises process economics. In addition to hydrogen, vast quantities of oxygen are produced by electrolysis of water. If a use were available for all this oxygen then of course it would have by-product credit but it would perhaps be unwise to do this for the speculative economy for which non-fossil chemical fuels are required. In the case of Fischer-Tropsch synthesis, some oxygen would be used in the plant itself.

Reference to Table 1 will show the dominant effect of the cost of the electric power on hydrogen: 80% of the hydrogen cost being represented by cost of the electricity. It is possible that this figure might be reduced slightly by improved electro-catalysis but at this stage it would seem unwise to make any such assumptions. Similarly, electricity at less than 4.0 mils/kWh would reduce costs. Nevertheless it is felt that this particular figure is as low as can be justified.

(b) Carbon Dioxide Production

In their work on liquid fuel synthesis using nuclear power in a mobile energy depot system by Steinberg and Beller [2], a proposal

was made to extract carbon dioxide from the atmosphere directly by compressing air, condensing water from it, drying the resultant air with a molecular sieve and finally extracting the carbon dioxide by another molecular sieve. Our attempts to calculate the cost of obtaining carbon dioxide by this means were halted by the realisation that the compressor costs would be simply enormous. The pressure vessels for the molecular sieves and the molecular sieves themselves would not be negligible in cost either. At the present time obvious sources of carbon dioxide are stack gases of fossil fuel power stations and the $CO_2$ exhaust from the hydrogen units of ammonia plants, hydrocrackers etc. However it is assumed that such sources will not be available in the same region in sufficient quantities to supply wholly synthetic fuel plants. A method which would avoid the need to pressurise the atmosphere would be to scrub the carbon dioxide from air by means of sodium or potassium hydroxide solution. It is difficult however to assign cost data to this process which has not been applied on any scale.

The process finally chosen for evaluation was to obtain carbon dioxide by calcining limestone rock and spreading the resultant calcium oxide back on the land. The quicklime would subsequently hydrate and finally carbonate by natural exposure to the elements. On this basis the synthetic fuel source is thought of as being situated near to a site from which carbonate rock could be mined and which provides plenty of land on which the resultant lime could be spread to weather for re-cycle. Clearly, if ever serious consideration were given to such a process, a considerable amount of experiment would be needed to determine its feasibility. For example, rates of carbonisation and dusting problems of the quick-lime would have to be evaluated. The costs given in Table 1 have been estimated from the costs of lime kilns in the U.K. Capital costs of 50% over those of a coal fired kiln were included to allow for a heat exchanger from nuclear heat. It is assumed that heat is available at half the cost of electricity i.e. 0.002/kWh. The alternative of electrical heating would increase overall costs by about 50%.

Some perspective on the amount of $CO_2$ available from the atmosphere for conversion to fuel is that the atmospheric reservoir of carbon dioxide appears to be about $2.5 \times 10^{12}$ tons [3]. As the concentration of carbon dioxide in the atmosphere is about 320 parts per million, each cubic kilometre of air contains roughly 430 tons of carbon dioxide. Because of the rapidity of air movements about the earth's surface the atmospheric system is fairly well stirred and one would not expect great difficulty due to lack of $CO_2$ in any particular area.
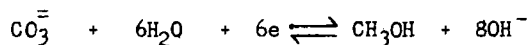
(c) Manufacture of Methanol

Methanol-synthesis is a well established industrial process. Feedstock for this process - as well as for the Fischer-Tropsch route - is a synthesis gas consisting of $H_2$ and CO in the ratio of about two, with minor amounts of $CO_2$ and $H_2O$. The CO is obtained from $CO_2$ by the reversed shift reaction

$$CO_2 + H_2 = H_2O \downarrow + CO$$
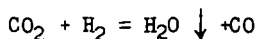
The latest low pressure processes have improved the economics of the Methanol-synthesis. Published data have been used to provide the figures summarised in Table 1.

Since one is talking about the future, it is interesting to speculate about an alternative process for the manufacture of methanol by means of the electrolysis of potassium carbonate. The authors are not aware of any data which show whether or not this process is in fact feasible, but were it to be so the following cathodic reaction could be expected to take place.

$$CO_3^= \; + \; 6H_2O \; + \; 6e \rightleftharpoons CH_3OH \; + \; 8OH^-$$

If indeed it were possible to carry out this reaction then it would not be necessary to manufacture hydrogen and one would have a wholly electrolytic process.

Materials of construction of the electrolysis plant for methanol would be similar to those for hydrogen–oxygen production since both involve an alkaline electrolyte and in each case the most corrosive conditions would be expected at the oxygen evolving anodes. On the other hand a stripper would be needed to remove methanol from the electrolyte and catalysts would be needed for the methanol electrodes. Some tentative figures for methanol production by this hypothetical process are included in Table 1. The assumption has been made that the plant would involve a 50% increase in capital cost over that for electrolysis of water.

(d)   Fischer–Tropsch Manufacture of Gasoline

Although gasoline would be the main product, other liquid fractions are obtained in the Fischer–Tropsch reaction. These are reflected in Table 1. Economics of the overall process have been described by Govaarts and Schutte [5] and their data have been used in preparing the relevant figures in Table 1.

TABLE 1

Rough economics for synthetic fuel manufacture (1970 basis)

| | Capital(1) employed 10^6 £ | Energy Consumed(2) (a) Electrical (b) Other energy MW | Manufacturing costs in 10^6 £/a | | | |
| --- | --- | --- | --- | --- | --- | --- |
| | | | All costs related (3) with capital (20% annual charge. | Energy costs 4£/MWh for Electricity, 2£/MWh for heat. | All other costs (4) | Total Manufacturing Costs |
| Electrolysis Water 3,300 T/d H (=1.1 10^6 T^2/a) | 250 | (a) 7,700 | 50 | 250 | 5 | 305 |
| CaCO$_3$ dissociation[a] 24,200 T/d CO$_2$ (=8.10^6 T/a) | 100 | (b) 2,900 | 20 | 45 | 20 | 85 |
| Methanol synthesis[b] 16,000 T/d methanol (=5.3 10^6 T/a) | 250 | (a) 300 (b) 350 | 50 | 15 | 10 | 75 |
| Total for Methanol route (5.3 10^6 T/a product) | 600 | 11,200 | 120 | 310 | 35 | 465 |
| Fischer-Tropsch synthesis c) 9,000 T/d F.T. gasoline (3.10^6 T/a) | 300 | (a) 200 (b) 800 | 60 | 20 | 15 | 95 |
| Total for Fischer-Tropsch route (3.10^6 T/a product) | 650 | 11,600 | 130 | 315 | 40 | 485 |
| Methanol via electrolysis (hypothetical) (5.3 10^6 T/a product) | 375 | (a) 7,700 | 75 | 250 | 15 | 340 |

(1), (2), (3), (4), (a), (b), (c) see Appendix A.

## III  Discussion of Results

Summarising the above results, one can state that liquid synthetic automotive fuels for present type engines can be made from $CO_2/H_2O$/energy at capital investments of roughly 650 $10^6$ $ for a plant to produce 3.$10^6$ T/a Fischer-Tropsch gasoline (or 5.3 $10^6$ T/a Methanol) at a thermal efficiency of 34%.  The manufacturing costs for Fischer-Tropsch gasoline would be about 160 $/ton (= 45 ¢/US gallon ≏ 450 ¢/MM BTU).  For methanol it amounts to 90 $/ton (= 30 ¢/US gallon ≏ 450 ¢/MM BTU).

Table 2 compares these results with:

(a)  the present situation in which gasoline is made with other products in a modern oil refinery,

(b)  a situation in the future, in which it is assumed that crude oil supply would be insufficient to meet the energy requirements, with consequential use of coal/tar sands/shale to fill the gap by converting these primary energy sources into synthetic methane, and crude oils (gasoline etc.).

The comparison made in Table 2 of course is only a rough one, but the data seem to be clear enough to make the conclusion that fossil primary fuels will be used preferentially for the manufacture of automotive fuels for existing engines and that the $CO_2/H_2O$/energy route has little chance to be competitive for a long time to come.

The above comparison is made on the basis of our present engines requiring specific fuels.  The cost and efficiency aspects were discussed of manufacturing these fuels from a variety of "primary energy sources".

As indicated in Table 1, the energy-efficiency of the manufacture of methanol and FT gasoline is only  34%  and these fuels are used in the engines with an efficiency around 15%; consequently, from the energy produced by the nuclear plant only about 5% is actually "used in traffic".

In Table 4 a comparison is made with the following routes, featuring "futuristic engines".

|  | Energy | Engine |
|---|---|---|
| A. | Nuclear energy ——— methanol | fuel cell/battery/electric motor |
| B. | Nuclear electrical energy ——— storage in batteries | battery/electric motor |

For the purpose of discussion it is assumed that batteries of 100 W/lb will be available at a cost of $20/kWh stored.  Efficiency charge to discharge of 50% is assumed.  This allows for electrode polarisation in a zinc-air battery or heat losses from a high temperature battery (e.g. sodium-sulphur).

In Europe it is found that gasoline service stations sell much more full at weekends in the four summer months than the mean throughput of the station.  In order not to overstress the disadvantages of batteries the figure of 50% overall utilisation of facilities will be assumed.  If batteries are exchanged at service stations, a day's store of energy will be needed to meet with fluctuating demands.  Distribution of electricity costs about $200/kW and a charger cost of $200/kW will also be assumed.  Bearing in mind the need for elaborate controls to ensure safety together with automatic handling of the batteries, this does not seem excessive.  It is interesting to note that a service station with the relatively modest throughput of a million US gallons a year (equivalent to a mean output of 600kW allowing for

## TABLE 2

### ROUTES TO PRODUCE AUTOMOTIVE FUELS FOR EXISTING VEHICLES

| Primary energy/conversion route/ "energy product" | Order of magnitude (1970) | | |
| --- | --- | --- | --- |
| | Capital for conversion process $/annual ton product [1] | Thermal efficiency conversion process | Manufacturing cost (exchange price) of product |
| As discussed above: methanol and FT-gasoline from $H_2O$/$CO_2$/energy (Data from Table 1) | 220 [2] | 34 | Methanol: 90 $/ton = 36 ¢/US gallon = 450 ¢/MM BTU<br><br>FT gasoline: 160 $/ton = 45 ¢/US gallon = 450 ¢/MM BTU |
| Present situation: gasoline/kerosine/gasoil from crude oils in modern complex refinery | 20-30 | 94 | Gasoline 9 ¢/US gallon = 90 ¢/MM BTU |
| Projected plants to convert coal [3] tar sands/shale into syncrudes (automotive fuels) and substitute natural gas (SNG) | SNG: 50-75 Syncrude: 60-100 | 65-75 | Manufacturing costs SNG: 70-100 ¢/MM BTU<br><br>Syncrudes: 3.5-6 $/bbl; 70-120 ¢/MM BTU |

1. Basis lower heating value products equivalent $10^4$ Kcal/Kg.
2. Excl. nuclear plant to produce electricity/heat.
3. Coal price in calculations: 12-17 ¢/MM BTU.

15% efficiency of the gasoline engine) would require a peak output of about 2.5MW. The energy stored in the station would be of the order of 30MW hours in batteries weighing a total of some 150 tons. Data pertaining to batteries are summarised in Table 3.

It will be noted from Table 1 that the electrolytic plant for hydrogen generation is a significant cost item. Perhaps surprisingly the total synthesis costs of gasoline is only little higher than methanol on an energy basis.

More revealing is the comparison of efficiency of energy conversion and capital cost per kW of mean throughput given in Table 4. As might be expected, the battery system has the highest overall efficiency but this factor is overshadowed by very high capital requirements. Even when the cost of nuclear power plant at an assumed $300/kW is added, the system looks most unattractive.

Despite the reasonable conversion efficiency of electrical energy to gasoline, the low efficiency of the gasoline engine gives rise to extremely high overall capital requirements. Some perspective on these figures can be gained from the fact that a Fischer-Tropsch conversion plant costs about $1000 kW available from a gasoline engine. This figure is so high that it makes the process unattractive. The best hope for synthetic fuels appears to lie in the use of methanol in a fuel cell(assumed efficiency with electric motor 50%). If electrolytic reduction of potassium carbonate solutions can be developed as an effective route to methanol synthesis this will clearly be more attractive than the existing chemical route.

One may conclude then that fossil fuels will be used for transport and other forms of "portable energy" for as long as they are economically available. If the methanol fuel cell is developed then fossil fuels will still remain the most attractive source of fuels for vehicles and other portable use. The high efficiency of the fuel cell will tend to prolong the life of fuel reserves. Ultimately when nuclear power is the major source of energy liquid fuels will still be available, albeit at higher prices than now.

## TABLE 3

### COST BREAKDOWN OF BATTERY STORAGE SYSTEM

| | |
|---|---|
| Distribution system | $200/kW |
| Rectifier and charger system | $200/kW |
| Batteries | $20/kW |
| Utilisation of distribution and charger | 50% |
| Efficiency charge to discharge | 50% |
| Batteries equivalent to 1 days peak output | 48 kW/hr/kW mean |
| Capital investment/kW distribution and charging | $800/kW |

## TABLE 4

### EFFICIENCY OF ENERGY CONVERSION AND CAPITAL INVESTMENT

| Fuel/Power Plant | Efficiency of conversion electrical to chemical Energy % 1 | Power Plant Efficiency % | Overall Efficiency % | Capital investment in plant ₵ per kW delivered | Capital plant + nuclear at ₵300/kW ₵ per kW delivered |
|---|---|---|---|---|---|
| Synthetic Methanol Table 1 | 34 | 50 $^2$ | 17 | 675 | 2,175 |
| Synthetic Gasoline Table 1 Gasoline Engine | 34 | 15 $^3$ | 5 | 2,660 | 7,660 |
| High Energy Battery | 50 | 90 $^4$ | 45 | 2,950 | 4,150 |

1. To compensate for the fact that thermal energy is assumed to be used in chemical synthesis, thermal energy is available at twice the "efficiency" of electrical energy; i.e. 1 kWh of thermal energy is equated to $\frac{1}{2}$ kWh electrical energy. Assuming electricity generation at 40% thermal efficiency, reactor heat is available at 80% efficiency.

2. Fuel Cell and Electric Motor.

3. Gasoline Engine.

4. Electric Motor.

## REFERENCES

1.  Costa R.L. and Grimes P.G., Chem. Eng. Progress $\underline{63}$ (4) 56-8 and Symposium Series.

2.  Steinberg M. and Beller M., Brookhaven National Laboratory Report, October, 1964.

3.  Nature $\underline{229}$ 514.

4.  Hydrocarbon Processing, September 1970, 277.

5.  Govaarts J.H. and Schutte C.W., 8th World Energy Conference, Bucharest 28th June - 2nd July 1971, Paper 3.3-187.

## DETAILS COST DATA TABLE 1

1.   Capital employed = Total erected plant ready for start-up, including all facilities and land and interest during construction and working capital (basis USA 1970).

2.   Energy consumed = All energy consumed in processes (minus minor quantity of energy produced by combustion of energy produced as by-products from synthesis routes). Electrical energy 4 Mils/kWh; heat 2 Mils/kWh.

3.   All costs which for costimating can be related with capital (in % of total capital investment, average over 15 years lifetime) : total 20%. This can be split-up as follows: depreciation 6.7%; return on investment (av.) 6.3%; all costs related with maintenance (supply, labour, supervision, overheads) averaged over 15 years = 4%; plant overhead (office supplies, R/D, accounting, legal, etc.) and property taxes and insurance = 3%.

4.   All other costs = Remaining fixed and variable costs such as Operating labour and supervision, chemicals and catalysts, utilities (excluding energy), royalties etc.

a)   $CaCO_3$ dissociation; 24,200 T3d $CO_2$

Energy consumed is twice dissociation energy of reaction $CaCO_3$    $CaO + CO_2$ (to take into account evaporation of water from $CaCO_3$ feedstock and heat efficiency of kiln). Assumption: heat available from nuclear plant at 900°C. Capital 50% higher than U.K. lime kilns with coal firing. Operating, stone handling and return at U.K. costs.

b)   Methanol synthesis; 16,000 T/d methanol

Capital in $/annual ton methanol

- ref. 4, complete train, incl. synthesis gas generation, scale 800 short ton/d           : 62 $/annual ton
- same, excluding synthesis gas plant    : 43 $/annual ton
- as reported in Table 1                  : 48 $/annual ton

Energy:

200 MWe for syngas compressors; 100 MWe for rest of plant, 300 MW heat.

c)   Fischer-Tropsch synthesis; 9,000 T/d gasoline

Capital in $/annual ton product

1.   As reported ref. 5 (including syngas plant), South Africa 1970: 200 $/annual ton.

2.   Same, but excluding coal handling, gasification, gas purification, part of steampower generation: 100 $/annual ton.

3.   Assumption that main product "gasoline" and by-products require same capital/annual ton product: this gives cap. requirement gasoline plant in Table 1: 100 $/annual ton.

Energy consumed

1.   As reported ref. 5: 200 MWe + 4000 MW heat for $2,510^6$ T/a plant.

2.   Assumed for our $3.10^6$ T/a plant (excluding the high energy consumption of the syngas part): 200 MWe + 800 MW heat.