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PRESENT STATUS AND TECHNO-ECONOMIC ASPECTS OF THE INDUSTRIAL PRODUCTION OF PETROPROTEINS $\frac{1}{2}$

by

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INTROD'ICTION

Micro-organisms which develop on hydrocarbons and on alkanes in particular have been known for a long time. But research on the production and use of these micro-organisms as a source of protein starded mainly in France in 1957, when the national laboratory of bacteriology and BP began to collaborate.

The objective was to select a micro-organism which could develop rapidly on cheap and abundantly available raw material such that a protein would be obtained with a reasonable methionine and lysine content and no sign of toxicity.

- Most yeast fermentations on alkanes have been tested. Two processes have resulted, namely:
 - the gas oil process: fermentation on a distillation cut $(250-400^{\circ}C)$ containing 10-15% of n paraffin $C_{15}^{-C}_{30}$ results in de-waxed gau oil and in a liomass of petroproteins
 - the n paraffin process: fermentation on purified n paraffin (98% C₁₀-C₁₈ corresponding to a distillation cut of 175-300°C), leads to a petroprotein which does not need to be extracted.

These two processes have been developed by several companies on pilot plant since 1963 and final products have been tested for food value and toxicity. For some months such products have been registered for use in animal feeds in most European countries*and in Japan. Some investment in commercial plant has been decided on, probably resulting in a total world production of 50 000 -

^{*} France, Germany, Italy

100 000 t by 1975.

- 2. Another research line has been developed by companies such as Shell and ICI from fermentation on natural gas and more recently on methanol. These processes seem promising for commercial production, but are still at the experimental stage.
- 3. Other research efforts using fermentation of yeast, bacteria and fungi on various sources of hydrocarbon and carbohydrate should also be mentioned at this stage. Raw materials such as molasses, lactoserum, citrus pulps and various industrial or agricultural wastes are being tested. Plant-leaf proteins and spirulina algae may also prove to be economic propositions for local production of protein.

In addition to the well-known worldwide need for nonconventional protein, the present dramatic price-increase and short supply of the main animal-feed protein sources such as fish meal, soya, groundnut, rapeseed, etc., would seem to favour the use of synthetic materials like urea, amino acids and petroproteins in particular. Petroprotein production technology is, however, rather complex, and several technical and economic factors should be weighed before taking a decision to invest.

THE PRESENT STATE OF PETROPROTEIN RESEARCH AND PRODUCTION

Present world production (including the socialist countries) is probably less than 50 000 t/year in the following pilot or semi-commercial plants (table 1). Several 100 000 t/year capacity units are expected to start operation by 1974-75, and production should reach 500 000 t/year by 1980.

EUROPE

The BP product called TOPRINA is sold in the UK at £220/ton mainly as a milk substitute for veal calves at the rate of 7% of the ration up to the age of six weeks and 10% thereafter. TOPRINA is also being used in the feed ration of broiler poultry (10-15%), turkeys (up to 10%), laying hens (15%) and piglets (up to 17%).

The demand for protein for animal feed is growing rapidly in Italy, France, the UK and Germany, and BP envisages installing a 100 000 t/year plant in each of these countries within the next few years.

The ITALPROTEIN* plant in Sardinia is now being built. This 100 000 t/year unit operating with n paraffin comprises three fermenters and will use a continuous process.

In the UK, a 100 000 t/year plant may be installed at Grangemouth, where a supply of n paraffin is available. A 4 000 t/year pilot plant is already in operation.

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COMPANY	LOCATION	ESTIMATED PRODUCTION t/year	
BP	LAVERA - FRANCE	16 000	
BP	GRANGEMOUTH - UK	4 000	
kyowa hakko kogyo	JAPAN	1 000-1 500	
KANEGAFUCHI	JAPAN	12 000	
DAINIPPON INK	JAPAN		
	USSR	10 000	
	CZECHOSLOVAKIA		
CHIA YEE SOLVENT WORKS, CHINESE PETROLEUM CO.	CHINA	500	

In France, the gas oil process will probably be used and registration has been obtained for the resulting petroprotein. A 100 000 t/year plant may be built at Lavera, where the 20 000 t/year semi-commercial plant is already in operation and where local animal-feed demand is growing rapidly. A further plant may be envisaged at Dunkirk which would also supply the Belgium market. For developing the gas oil process BP has obtained subsidies from the Agricultural Fund of the EEC and from the French government, as this product will replace imported proteins.

In Italy, LIQUICHIMICA BIOSINTESI envisages the production of petroprotein at their fermentation plant complex in Sicily, where citric acid, amino acids and fatty acids will also be produced. This company has a licence from KANEGAFUCHI and will benefit from a large local supply of n paraffin. It seems that the Kanegafuchi process could use the citric acid production plant, which would lower the break-even point of petroprotein production. Fermentation would be carried out in 20 fermenters of 600 m³ each (100 000 t/year).

In Europe, several more pilot plants are being considered by Shell, ICI and IFP-CFP-ELF-ERAP, but no consistent production has so far been mentioned. Commercial production by ICI using the methanol process is not expected to begin for several years.

THE U.S.A.

Probably due to a less dramatic protein gap and to the increasing pressure of soya bean producers, American companies have not been stimulated to develop petroprotein production processes in the same way as their European or Japanese competitors. However, the Northern Illinois Gas Co. (NIGAS) has developed a process on natural gas. GULF and HERCULES (methanol process), MOBIL OIL (gas process), PHILIPS-GENERAL MILLS, and AMERICAN SUN are also considering petroprotein production.

ESSO-NESTLE has developed a process on ethanol leading to a high-purity protein which could be used for human food. However, no registration for petroprotein has been given so far.

JAPAN

In Japan several companies have developed petroprotein processes during the last ten years in order to fill the large and rapidly growing animal-feed protein gap.

BP has licensed the n paraffin process to KYOWA HAKKO KOGYO CO., which has very recently been accorded registration by the Japanese government but is delaying building a plant (100 000 t/year).

KANEGAFUCHI CHEMICAL CO. and DAINIPPON INK & CHEMICALS have developed their own n paraffin process but seem to be having difficulty in obtaining registration. They plan two 60 000 t/year plants, but could be forced to abandon this project because of consumer opposition movements. Other companies such as SUMITOMO CHEMICAL CO., ASAHI CHEMICAL CO. and MITSUI TOATSU CHEMICAL CO. (gas oil process) are also considering petroprotein production.

DEVELOPING COUNTRIES

Joint ventures between Japanese companies and developing countries seem to be progressing favourably. DAINIPPON INK & CHEMICALS CO. recently announced that it has reached a mutual agreement with SUMITOMO SHOJI KAISHA on a plan to sell petroprotein manufacturing technology to MICH of ROMANIA and to start up a joint venture there. Romanian n paraffin could then be used in this 60 000 t/year plant, which should be built by 1974.

Local petroprotein production projects have been mentioned. Among them is that of the CHIA YEE SOLVENT WORKS and the CHINESE PETROLEUM CO., which are now running a 500 t/year pilot plant.

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In India, several projects are being considered (i.e. by the Indian Oil Co. in collaboration with the GROUPEMENT FRANCAIS DES PROTEINES).

SOCIALIST COUNTRIES

It has been reported that the USSR already has a production plant using the natural gas process. The BP n alkane process seems to have been adopted in Czechoslovakia where a 20 000 -30 000 t/year plant is thought to be in operation.

TECHNICAL ASPECTS OF PETROPROTEIN PRODUCTION

All industrial experts agree that petroprotein production processes are complex and, that after laboratory processes have been scaled up to 100 000 t/year in the new factories further problems will certainly emerge.

All known petroprotein manufacturing processes consist of three or four major steps requiring highly qualified fermentation specialists and biochemists, plus well-equipped laboratories. These main steps are:

- 1. purification and sterilization of raw materials
- sophisticated control of fermentation parameters (Te, PH, mixing etc.)
- 3. extraction of the crude petroprotein
- 4. purification, drying and analyses.

Process conditions vary greatly with feedstocks, and technical difficulties are specific to each process (see table 2).

Gas oil and n paraffin processes

The gas oil and n paraffin processes both use CANDIDA yeast, and fermentation is carried out with a two-phase mixture, the yield being about one t of product per t of n alkane consumed. Processes are continuous, and oxygen, ammonia, phosphoric acid

and mineral ingredients are metered automatically. The main problem for these two processes is to keep the fermentation temperature at 30[°]C with very high-capacity external heat-exchangers and careful mixing as 7.5 Kcal are generated per gram of crude protein product.

Gas_oil_process

This process is based on gas oil feedstocks and does not exclude atmospheric contaminants.

Suspension is acidic (PH 4) to prevent growth of bacteria which would compete for nutrients and contaminate the final product. There are no risks of contamination if the PH is carefully controlled. The mixture is decanted and aerated. Centrifugation then leads to a biomass of protein which is purified by counter-current solvent extraction and dried.

The purification step is certainly the most difficult part of this process, as all traces of gas oil and carcinogenic aromatic derivatives (benzo pyrene) must be washed out. It leads to a product of 66% dry weight which in practice does not contain lipids.

n paraffin process

It is interesting to note that, in some articles published in the early 1960s, protein concentrate was considered a by-product of deparaffinating by micro-organism. In fact the cost of this biological purification was almost twice that of the molecular sieve method (about E2/t).

The BP process requires 98% pure n alkane and needs aseptic conditions. The C_{10} - C_{18} alkanes are produced from certain kerosene fractions (mainly Libyan crude) by molecular sieve. Filters, sterilization units and welded plant eliminate contamination in this process, in which the yeast suspension is neutral.

The KANEGAFUCHI process uses $C_9 - C_{19}$ n paraffins (instead of $C_{10} - C_{18}$ as in the case of the BP and DAIN1PPON INK processes) and the yield is claimed to be higher. The final product should contain less ppm of polyaromatic derivates.

Methanol process

Little is known about this process. Fermentation seems to be easier to control than in the case of hydrocarbon processes, and proteins are extracted by simple washing with water.

Methane process

The advantages of using a methane feedstock include the fact that the product protein needs only an aqueous wash and that the process need not be run under aseptic conditions.

The source of nitrogen is ammonium nitrate. The methane process uses bacteria instead of yeast. Yeast has a larger

particle size, is easier to collect, and grows at lower PH value than bacteria, which reduces the possibility of contamination. Bacteria have a lower lysine content but lead to higher protein concentration, are faster to grow and simpler to prepare in a culture medium than yeast. Bacteria lead to a more palatable product which could probably be used for human food, and which will be ready for commercial production by 1980. At present, Shell is operating two 300 litre continuous fermenters and would like to expand to a pilot plant capable of producing more than 1000 t/year.

ADAPTATION OF THESE PROCESSES TO DEVELOPING COUNTRIES

To be economic these processes must be continuous, which calls for very sophisticated control of the fermentation parameters. Furthermore, the final product must be consistent. This necessitates careful purification, respecially if the gas oil process is used.

These production processes require a power station to supply energy to the cooling unit, and also a steam boiler if the process calls for sterilization of raw materials and plant (as in the n alkane process).

Large commercial factories are not yet in operation, but there is no doubt that the criticality of the processes will necessitate a permanent staff of very highly qualified biochemists and fermentation specialists who will be most efficiently be employed in a large fermentation plant complex such as Liquichimica's.

On the basis of their technical aspects, it would appear that these processes have been developed for industrial countries where water temperature is often between 10 and 25° C and where sophisticated staff are already available. A second-generation plant of smaller capacity using micro-organism fermentation at more than 30° C and requiring less aseptic conditions and purification would be better adapted to the manufacturing potential of the more advanced developing countries. Nevertheless, it seems that the gas oil process would be at the moment more economically adaptable to 20 000 t/year plant than the n paraffin one.

ECONOMIC ASPECTS OF PETROPROTEIN PRODUCTION

Investment and production cost

The present price of BP's petroprotein is £220/t and it has been suggested that this should come down to £150/t when commercial plant comes into operation.

Capital investment and production cost figures have been cited in various articles, but most manufacturers agree that before commercial production begins it is difficult to make precise estimates, as many unexpected increases in capital cost tend to occur during the scaling up of such sophisticated processes.

However, it does appear that the investment for a 100 000 t plant using the gas oil process would be lower than that for one using the n paraffin process, which has been estimated at £25 million.^{*} The methanol process investment has been underestimated at £15 million, and the investment for the methane process would probably be under £20 million for the same size.

It is clear that these processes are capital rather than labour intensive. Production costs are more difficult to estimate and depend on the local price of raw materials and energy. However, they would be higher for the gas oil process, and there is some possibility that with the methanol process production costs could be competitive with the n paraffin process.

The cost items for n paraffin and gas oil processes as percentages of total manufacturing cost are given in table 3 (BP figures).

^{*} probably due to the cost of equipment needed for ensuring aseptic conditions.

	n paraffin process GRANGEMOUTH	gas oil process LAVERA
Raw material	478	408
Utilities	13%	15%
Labour Maintenance Overheads Depreciation)) 40%)	458

TABLE 3

Raw materials

As Table 3 shows, the economics of production are mainly related to the price of raw material. It is most likely that, in the search for cheaper ones, future research efforts will covera wider range. Here, however, we shall concentrate on gas oil, n alkane, methanol and methane.

Gas oil

n paraffin-rich gas oil is widely available, but the n paraffin content varies greatly according to the origin of the crude oil. Indonesia, Iran and Libya are the usual sources.

With the rapidly growing demand for energy, the price of gas oil is bound to continue increasing in industrialized countries. The internal transfer price will remain the same in most of the oil-producing countries, which could be an incentive for them

to produce petroproteins from gas oil.

n paruffin

n paraffin will remain relatively independent of the increasing price of energy and the supply will certainly satisfy the demand for biodegradable detergents.

A refinery with a refining capacity of 100 000 EPSD* would be capable of producing 24 000 t/year of n paraffin C_{14} - C_{18} . So one refinery is generally not enough to supply the needs of a 100 000 t petroprotein factory.

In Japan, the KANEGAFUCHI and DAINIPPON INK petroprotein plant will be fed with a paraffin from NIERO PETROCHEMICAL and (mainly) from imports. Other Japanese petroprotein producers will be in the same position. From the quantity viewpoint, Japan has sufficient production facilities for a paraffin (141 000 t/year) but quality wise there is not enough capacit, for the petroprotein plants. NIPPON MINING produces 40 000 t/year of suitable a paraffin and will expand to 70 000 t/year using the NUREX process. A new 100 000 t/year plant is planned by TONEN SEKIYU KAGAKU with the ESSO process.

In Europe petroprotein manufacturers are also producing n paraffin. BP has n-paraffin extraction plants in the UK and the Netherlands. LIQUICHIMICA is in an excellent position, as its n paraffin production capacity is between 500 000 and 600 000 t, corresponding to the 45 million t of Libyan crude refined by Esso, Montedison and ISEB in Italy. This large capacity reduces the cost of producing n paraffin, which may render their product very competitive with BP petroprotein.

barrels per stream day

Methanol

1

The price of methanol is going down owing to increasing plant capacity. The production cost is estimated to be about \$32/t in Europe, of which 30% is the cost of natural gas, and \$25/t in the United States, of which 20% is the cost of natural gas. Methanol manufacture from naphtha leads to a higher production cost of about \$42/t in the USA and \$37/t in Europe and Japan for a 725 t/day capacity plant.

Table 4 shows Battelle estimates of the methanol plants to be installed in various countries by 1975 and 1980. It is interesting to see that several large-capacity factories are probably going to be built in Brazil, Iran, Libya, South Africa and China. This could be favourable to the local production of petroproteins, as this process seems to lead to fewer technological problems than other hydrocarbon processes.

If the internal transfer price of methanol is lower than \$40/t this will lead to a very competitive petroprotein.

Methane

As the price of gas oil will tend to increase, more natural gas will be used. The price of the latter may thus exceed the estimate of \$5/t in certain countries.

It is obvious that if the technological problems of the methane process can be solved, the production cost of these proteins will become very competitive relative to the gas oil or n paraffin processes.

MARKETING ASPECTS

In industrialized countries, biosynthetic protein production has become an economic proposition when it can compete with conventional sources of proteins, especially high-quality ones such as fish meal, of which approximately 80% of the demand has a high price elasticity.

The first item to consider in the siting of these plants is the meat production capacity and its growth. This is why investment in production plant was first decided on in France, Italy and the UK.

Moreover, owing to specific registration procedures, these petroproteins might be difficult to import from a country where the process and raw material are different.

In developing countries the animal-protein deficiency is already acute and will probably double or triple in the next 20 years. It is generally accepted that the minimum amount of protein per day for proper human nutrition is 70 g, of which at least 20 g should be animal protein containing essential amino acids. FAO has estimated that at present the average daily intake of animal protein per capita in developing countries is no more than 12 g. In these conditions, return on investment should obviously not be the first criteria of a feasibility study on a petroprotein plant. Nevertheless, the per unit production cost of petroprotein should be competitive with the potential local source of natural protein, for example fish meal or groundnut cake, which require much less investment and technology to produce.

In any plant feasibility study, marketing criteria also have to be considered. Petroproteins have to be used in the correct proportions, and cannot therefore be sold directly to the farmer. This means that compound feed industry must exist. This, in turn, implies a large demand for intensive animal production and a good distribution structure.

If petroproteins are added to the ration at an average rate of 10%, a 200 000 t/year compound-feed industry would be needed to absorb 20 000 t of petroprotein. This would lead to a production of 56 000 t of broilers and 55 000 t of eggs, which could feed a population of 19 million at a per capita annual rate of 3 kg of chicken and 3 kg of eggs. These figures were calculated in a feasibility study for a North African country carried out by Battelle.

Most of the advanced developing countries do not have a 100 000 t/year coumpound-feed industry. Nevertheless, before drawing any definite conclusions as to the feasibility of petroprotein production, several advantages of local production should also be weighed, namely:

- reduction of animal and vegetable protein imports
 leading to foreign currency savings
- use of locally produced or available raw material such as gas oil, methanol or methane
- export of petroprotein as a source of foreign currency
- stimulation of local animal production
- stimulation of local chemical industry to invest in other fermentation processes.

CONCLUSION

- 1. In order to forecast the petroprotein demand and supply situation beyond 1980 in industrialized countries it is important to take the following factors into account:
 - the petroleum industry's need to diversify will increase
 - the recovery of resources will become more vital and large companies such as Union Carbide and Air
 Products will develop waste-disposal processes
 - the cost of energy will greatly increase
 - the demand for biosynthetic protein for animal production will compete with demand for human use, and the price of natural proteins will increase.

The ideal process for producing protein would thus:

- be a waste-recycling fermentation system
 (agricultural or industrial waste)
- use bacteria developing at over 30°C
- consume little energy.

At present recovery processes are too expensive to be competitive (between \$530-710/t) and the supply of raw materials is too unreliable.

Nevertheless such a process does not seem unrealistic when we consider the rapid progress of fermentation engineering.

In the United States, a digital computer has been successfully combined with an instrumental pilot-plant fermenter at SQUIBE's Biological Process Department to explor and optimize biochemical processes. Soviet scientists plan to use this system to develop biosynthetic protein.

Several processes for converting a variety of waste-products into food are being studied. In 1969 the Swedish Sugar Co. announced a process for treating a potato-starch-filled waste stream with candida yeasts. Louisiana State University has developed a new breed of micro-organisms that can be cultured on sugar-mill pulp, leaves, corn cobs, rice hulls, wheat or sawdust. In several parts of the world other processes are now being developed to generate protein from local raw materials or wastes (hydrocarbons, carbohydrates, etc.). Some of these small plant processes are said to provide a good return on investment.

2. As yet, all petroprotein production processes should be considered experimental as large-scale commercial production has not yet started. Before drawing final conclusions concerning the possible transfer of this technology to developing countries, difficulties of these processes and alternative sources of proteins should be carefully studied.

To run these plants (whether gas oil, methanol or methane processes) a very high level of expertise in fermentation and in micro-biology will be permanently required, and this could be considered as the major obstacle to local production in some of the more advanced developing countries. Another difficulty is the large investment required.

Production costs and commercial outlets could be considered as less important in certain of these countries.

As petroprotein contains less than 3 g of methionine for 16 g of nitrogen it needs to be enriched with methionine, which is probably the most essential amino acid in developing countries. It is an open question whether production of methionine itself should not be given higher priority, as it could supplement local sources of vegetable protein (manioc, farinaceous products, root crops, etc.).

Developing countries could well consider certain alternative forms of protein production, particularly where refineries do not exist.

2.1 Processes on agricultural products and wastes have been tested (e.g. manioc, molasses, citrus pulps and bananas) and the UNIDO attempt to develop fermentation on cyprus cubes is encouraging.

> The spirulina algae process developed by IFP in Mexico would be a model to follow. Proteins from spirulina algae contain amino acids essential for animal or human nutrition, but their industrial production needs improvement, especially as regards the protein extraction step.

2.2 Synthetic or processed proteins which could be used directly for human food might well be preferred to protein for animal feed, especially in developing countries where animal production is not intensive.

Since 1965 ESSO NESTLE have been developing a fermentation process on ethanol leading to a high quality protein for human food - but nothing has been published concerning its economics.

In the UK, the RANK HOVIS process of fusarium mold fermentation from various agricultural wastes, molasses, lactose, etc., leads to a protein for human food. A 20 000 t/year plant could feed about half a million persons and would require 1200 ha of manioc or 3200 ha of sugar cane.

Companies	BP Mitsui toatsu	BP KANEGAFUCHI DAINIPPON INK GULF OIL	ICI HERCULES MOBIL OIL KAROLINSKA INSTITUTE	SHELL NORTHERN ILLINOIS GAS CO
PROCESS	GAS-OIL (10% n alkane)	N PARAFFIN 988 (C ₁₀ -C ₁₈)	METHANOL	METHANE
Micro-organisms	Candida Yeast	Candida Yeast	Bacteria Yoast	Bacteria (Methanomonas, Pseudomonas sp)
Raw materials availability	Very large supply	Large supply is expected in Europe - short supply in Japan	Large methanol plant capacity	Very large availability
Price trend	\$40/t	f60/t in Europe \$114/t in USA & Japan	Decreasing from \$100 to \$40 per tom	\$5/t
Yield	0,85-lt/lt n paraffin contained in gas oil	lt/lt n paraffin	0,40t/1 t methanol	0,25t/lt methane/. lt oxygen
Concent rat ion	661	631	751	701
Lysine	7,8g/16g of N	7,4g/16g of N		
Methionine	1, 6 g/16g of N	1,8g/16g of N		deficiency in methionin
Production difficulties	PH 4-6 to control	PH 7 to control		extraction of smaller bacteria is difficult
	cooling centrifugation extraction,	aseptic conditions cooling		contamination hazards explosion hasards
	purification high risk of contamination of final product			(oxygen + methane) poor yield
Invest me nt	about £20 millión	£25 million	ElS million (underestimated)	E 20 million
Production cost		Price: E220-150 should be more economic than gas oil	future production cost may decrease from \$430 to \$250/t and could become more economic than the n paraffin process	production cost is estimated at \$525/t

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TABLE 4

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