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UNITED NATIONS INDUSTRIAL DEVELOPMENT ORGANIZATION
Vienna International Centre, P.O. Box 300, 1400 Vienna, Austria
Tel: (+43-1) 26026-0 · www.unido.org · unido@unido.org

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PRODUCTS OF PHOTOSYNTHESIS AS RAW MATERIAL FOR THE CHEMICAL INDUSTRY*

by

P. Dupuy**

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** Institut National de la Recherche Agronomique, 7, rue Sully, 21 034 Dijon, France

Ten years ago, different meetings were examining the possibility of substituting oil for feedstocks of biological origin utilized in the fiber, feed and food industry. At this time, we are examining the reverse situation. It is not necessary to judge the later proposition as better than the former, because it seems preferable to have in hand both techniques, With the choice dependend upon economic circumstances.

Developments of the organic chemical industry have heretofore been based on utilization of coal. Now, natural gas and crude oil supply the chemical industry with feedstock and energy.

Although the demand for feedstock is growing, 3-5% per year,the production of oil will reach a maximum between 1980-1990. The prices of these products are more uncertain than the level of their production. These changeable circumstances can alter considerably the situation of the chemical industry.

The introduction of renewable carbon sources as a feed-stock is now being investigated by several companies of the petrochemical industry and supported by energy programs of governmental organizations.

EXISTING RESOURCES

The immense world production of photosynthesis, which is 150 10^9 tons/year far exceeds the needs of the chemical industry, and only 5% of this large biomass would be necessary to meet the present demand for oil and gas. The part of biomass which will be used as industrial feedstock appears very small and it cannot really affect the other utilization:

- food for humans,
- feed for animals,
- restitution to the soil of organic matter in order to maintain fertility.

These resources are difficult to collect and in some cases it would be better to develop special efficient and economical productions, known as energy farming. Further it is surprising to note that in some countries the needs of the chemical industry could be satisfied through cultivation of a small percentage of the ground. For the U.S.A.,the figure is about 6%.

This energy farming is of course not possible in certain countries because of their low natural production resulting from dryness or cold climate. For still others the priority use of their available soil for food production is certainly a limitation.

Agriculture also produces a large quantity of wastes, some of which are merely lost without benefit to man, while still others are pollutants requiring energy for their elimination. Whenever possible these must be changed into useful by-products.

Some of these wastes are already available in large quantities such as straw, molasses, bagasses and also leaves, branches and bark which are left in the forest.

In the U.S.A. for example, the amount of synthetic material, fibers and rubber produced annually is 18 million tons. About 95% could be obtained from wood, if necessary, and the amount of feedstock would be 60 million tons. The amount of wood pulp now produced annually requires 100 million tons of wood. Under these circumstances, the demand of wood for chemical industry appears modest, and could be met by the residues now unemployed :

- 50 million tons found in the logging residues left in the forest,
- 15 million tons found in the manufacturing residues burnt in the plants.

Many countries have a large surface of hardwood of poor quality which is unemployed because the wood pulp industry requires long fibers cellulose. This green junk could be used as chemical feedstock leaving the ground clear for a cultivated and genetically improved forest.

CHEMICAL NATURE OF BIOMASS

Biomass is 10 to 80% water, which makes transportation expensive and storage sometimes difficult. The ash content is reasonably low, less than coal. This ash can be used as fertilizer. The amount of organic sulfur is very low which is an advantage over oil and gas which must be desulfurized before their chemical use.

Four types of polymers present in vegetals are being considered for their industrial use (fig. 1).

- Cellulose is a β 1-4 glucane, which is in many cases 30%, (even 50% in wood) of the dry matter of the vegetal. Its hydrolysis, chemical or enzymatic, is difficult because of the β linkage.

- Hemicellulose contains different classes of polymer, especially pentosanes which give furfural. Hemicellusole can reach 25% of the vegetal.

- Starch (α 1-4, α 1-6 glucane) accumulates only in cultivated plants and in special organs where it reaches high concentration. Its hydrolysis chemical or enzymatic is easy.

- Lignin is a phenylpropane polymer. As opposed to the other polymers which are in chain arrangement, lignin has a three dimension arrangement with various proportion of cross-linkage. In wood, it can exceed 30% by weight.

The economic utilization of this biomass, which contains different classes of chemicals, requires processes able to valorize all of them.
In a large factory , it is not possible to leave a part of the material accumulating as waste, because it will become rapidly an environmental problem.

BIOMASS HYDROLISIS

This process is necessary to obtain the basic molecules which will be valorized by industrial chemistry. Previously hydrolysis was utilized in variou countries on various raw material. Then, plants which could not survive war economy, were closed except those of U.S.S.R. They were 20 in 1960, now 35 are in operation producing feed yeasts and furfural .

- Meunier's process uses sulfuric acid at a concentration of 1,8 to 2,5 for 20-30 minutes at 175°. The attack can be repeated. The process has been used in France. In a recent evaluation, it still seemed promising.

- Scholler's process places the material in a large reactor of 50 m3, heated by steam to 125°C and percolated by sulfuric acid at a concentration of 1%. The attack is repeated 15 times increasing the temperature to 170°C and decreasing the acid concentration. There is a better yield than in the Meunier's process, but it works slowly and acid is also lost because it must be neutralized.

- Bergius's process produces hydrolysis by hydrochloric acid. The raw material submitted to 1% solution at 100° C gives a solution of glucose tetramere. After washing the attack is repeated for 40 hours. Hydrochloric acid is recovered by distillation. It is necessary to heat the sirups to115 with the hydrochloric acid at 3% in order to hydrolyse the tetramere. The yield of the process is very high, close to the theoretical maximum.

With a modification of this process hydrolysis can occur using hydrochloric acid in vapor form (Hereng process). A pilot has been built by BATTELE GENEVA in order to reevaluate the economy of this process.

All these processes produce, in addition to glucose, a certain amount of furfural, acetic acid, and methanol, with lignin as a residue, if it is present in the raw material.

The need for research to improve the hydrolysis process is evident, especially

- to reduce corrosion,
- to obtain a more satisfactory handling of the solid,
- to integrate the process with other chemical industry, for example fertilizer manufacturing.

Cellulose hydrolysis is a very difficult procedure because the rate of glucose destruction is of the same order of magnitude as the rate of hydrolysis. This is a major deterrent to a wood based chemical industry. The facility of hydrolysis of cellulose occuring in natural material depends on

- the extent of lignification,
- the degree of crystallinity.

In order to facilitate hydrolysis, pretreatments are possible :

- digestion with soda or ammonia,
- woodchip piled and inoculated with molds or enzymes.

LIGNIN UTILIZATION

The chemical structure of lignin differs considerably from the other polymers formed in vegetal because the arrangement of the units of phenylpropane occurs in three dimensions and not as linear or branched polymers.

At the present time, lignin appears in all the processes as a by-product and either remains in the residues of hydrolysis or is extracted as a liquid in the black liquors of the paper industry. After dewatering lignin can be burned with a caloric value of 5 800 c/Kg and can thus produce steam necessary in all industry.

It would be better to depolymerise lignin and to recover phenols. These molecules from oil origin are already used in chemical industry and especia ly in polymer synthesis. Hydrogenolysis at high pressure, 170 Atm, and high temperature, 450°C (Nogushi process) gives a wide spectrum of phenols which are difficult to separate.

Lignin can when demetylated also be used to produce phenol-formol polymers, known as thermosetting resins.The mechanical properties of these resins are not known and it is difficult to compare their value and price to other synthetic resins.

Lignin remains a subject for academic and industrial research.

THE INDUSTRIAL ROUTES

There are three main routes to introduce chemicals obtained from biomass into the chemical industry : Ethanol, Furfural and Methanol route.

Ethanol route

The production of ethanol through the fermentation of glucose is a simple operation, however because of the loss thereby of 1/3 th of the carbon in form of CO2, the yield is poor. Recovery of ethanol by distillation is an economical operation requiring only 18% of its energy.

Ethanol can be used as a feedstock for production of many chemicals, even synthetic fibers and rubber.

Ethanol is presently produced by synthesis or by fermentation of agricultura by-products. The ratio between both origins would depend on a given country's policy. The part of the ethanol of agricultural origin is 100% in BRAZIL, 70% in FRANCE and only 20% in the U.S.A..

The process of conversion of sugar into ethanol and its recovery is much more advantageous than alcohol synthesis. The cost of conversion to obtain 1 gallon of ethanol has been estimated as follows :

Fermentation	13,7 cents a gallon
Synthesis	21,5 cents a gallon

The difference in the price of the product depends on the price of the feedstock used . If ethylene at 15 c/lb is used the price of the feedstock is 4x15 = 60 c/gal. If molasses at 60 $/t is used the price of the feedstock is 72 c/gal.

A much lower price could be obtained if an integrated chemistry of vegetal material could be achieved.

The figure 2 shows the different molecules which could be obtained from ethanol.

1 - The reduction of ethanol to acetaldehyde is a commercial operation. The capacity of these plants has reached 300 000 t/per year in 1974. These units are however underemployed because the direct hydration of ethylene is more economical.

2 - Dehydration of ethanol to produce ethylene is the only source of ethylene in some developing countries ; however, their need for ethylene will remain low for many years to come.

3 - Acrylonitrile is a major constituant of fibers.

4 - Acetic anhydride is mainly utilized to produce cellulose acetate.

5 - The production of vinylacetate which has been operated by Celanese, has been discontinued because acetylene is a less expensive feedstock.

6 - The production through this reaction of butadiene, the base for synthetic rubber, has been discontinued by this reaction because its synthesis is possible from the C_4 cuts which has had, until now, limited utilization.

A major advantage of a chemistry based on ethanol is that all the transformations have already been carried out on an industrial scale. Another interest is the possibility introducing interchangably ethanol from both ethylene or vegetal.

Furfural route

At the present time, furfural's main use is as a solvent in the productio of lubricating oil. A polymer of furane has been produced on an experimental basis and used as binding material in concrete.

The use of furfural as a feedstock for chemistry is being investigated by different chemical companies, especially by DUPONT DE NEMOURS, because it conducts to nylon. This chemistry does not have an industrial background but new routes appear for chemicals of large utilization. Furfural cannot be synthesize from oil. Its route is a new one and it can be opened only if the price falls much lower than the actual figure, $ 800 a ton. This is possible if the hexoses produced during the preparation of furfural can be valorized by alcoholic fermentation or yeast production.

The figure 3 shows the different chemicals which can be produced from furfural. Production of polymers of the nylon type is the most promising issue.

Adipic acid could be obtained by carbonylation of tetra hydrofurane. This process is currently in the pilot plant stage.

Different types of nylon are obtained by polymerization of butyrolactam (nylon 4) or valerolactam (nylon 5). It seems that nylon 6 cannot be produced at a competitive price in this manner because the chain-lengthenir stage for obtaining caprolactam is too expensive.

The production, by a catalytic oxydation for furfural, of maleic anydrid which used to obtain polyester resins,is now in the pilot plant stage.

As opposed to ethanol route, furfural route lacks industrial background.

Methanol route

This route is interesting beccause methanol can be produced from different feedstocks,as shown in figure 4.

Oil or coal burnt in presence of water and with an oxygen deficiency gives a mixture of CO_2, CO and H_2, the synthesis gas, which gas can also be obtained by the combustion of methane coming from natural gas. The most volatile fractions of natural gas are used in this way through the reforming reactions.

Biomass can contribute in the production of synthesis gas in two ways.

1. The first is the methanic fermentation. This is a complex process of bioconversion which requires different activities :

- hydrolysis of cellulose,
- production of volatile acid,
- anaerobic production of methane and CO2.

This mean of methane production is chiefly used to produce energy. Its advantage is the possibility of operating small installations and the use of a large range of substrates, including manure, straw, muds from sewages ponds, etc...This fermentation can be obtained in fermentors or in landfil wastes disposal, in which case, it is possible to recover a gas of 50% methane. A demonstration of the feasibility of this production is being done in California.

2. The second way is pyrolysis, which is the combustion of organic material in an oxygen-deficient environment. When applied to wood, this technique gives different products :

- methanol (wood alcohol)
- acetic acid
- formic acid
- acetone
- charcoal

Some gas plant are still in operation.

Applied to urban refuse, this technique produces oil, char, low calorie gas, etc... In all these systems, gas is converted into energy, heat or electricity. Experimental plants have been developped in U.S.A. with capacities of up to 1 000 T/a day.

- GARRET RESEARCH AND DEPARTMENT CO.
  flash pyrolysis
  200 t/day
  SAN DIEGO CALIFORNIA

- UNION CARBIDE
  burning in pure oxygen to improve the energy contained in the gas
  200 t/day
  SOUTH CHARLESTON VIRGINIA

- MONSANTO ENVIRO-CHEM
  oil heated rotary kiln
  1000 t/day
  BALTIMORE

Hydrogenation of synthesis gas produces methanol (fig 4), which is a basic inexpensive molecule which is used for

- reduction in formaldehyde,
- synthetizing acetic acid,
- fermentation by microorganisms to produce singel-cell proteins.

The methanol route appears best way for obtaining energy from biomass an can also be used to produce basic chemicals.

Many other possibilities exist for preparing useful chemicals from vegetal material, but they have limited utilization compared to the large possibilities of the main routes we have reviewed . For exemple, the following can be mentioned: turpentin, vanillin, xylitol, sorbitol, mannitol ...

CONCLUSION

Some years ago the topic of this paper would seem rather academic . Recent events prove that it is now a deep concern for the chemical industry .

The Seminar on the Residues Utilization and Management of Agricultural and Agro-Agricultural Wastes convened by FAO and United Nation Program for Environment, Roma Januar 1977, has been attended by representatives of the following chemical and petroleum interests: SONATRACH (Algeria), HERCULES (USA), SHELL INTERNATIONAL, RHONE-POULENC (France), ASAHI CHEMICAL (Japan), MITSUI (Japan) .

In july 1977 a conference convened in Toronto by CHEMRAWN and IUPAC has spelled out those factors "that will ultimately determine sources of organic raw materials necessary to support world chemical industries at the end of the century" .

Ethanol is one of this raw mateials . We have an old industrial experience of its production . It can be produced in small plants which is now an advantage to minimize the problems of environment .

It is necessary to combine its production with the valorization of the other parts of the biomass .

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Fig. 1 Conversion of Natural Polymers into Basic Intermediates

Polymer	Hydrolysis	Hydrolysis		Pyrolysis
		by chemicals	by enzymes	
Starch	easy	industrial	industrial	—
Hemicellulose	less easy	industrial	—	industrial
Cellulose	difficult	industrial	pilot plant	industrial
Lignin	very difficult	—	—	industrial

Fig. 2

Ethanol Route

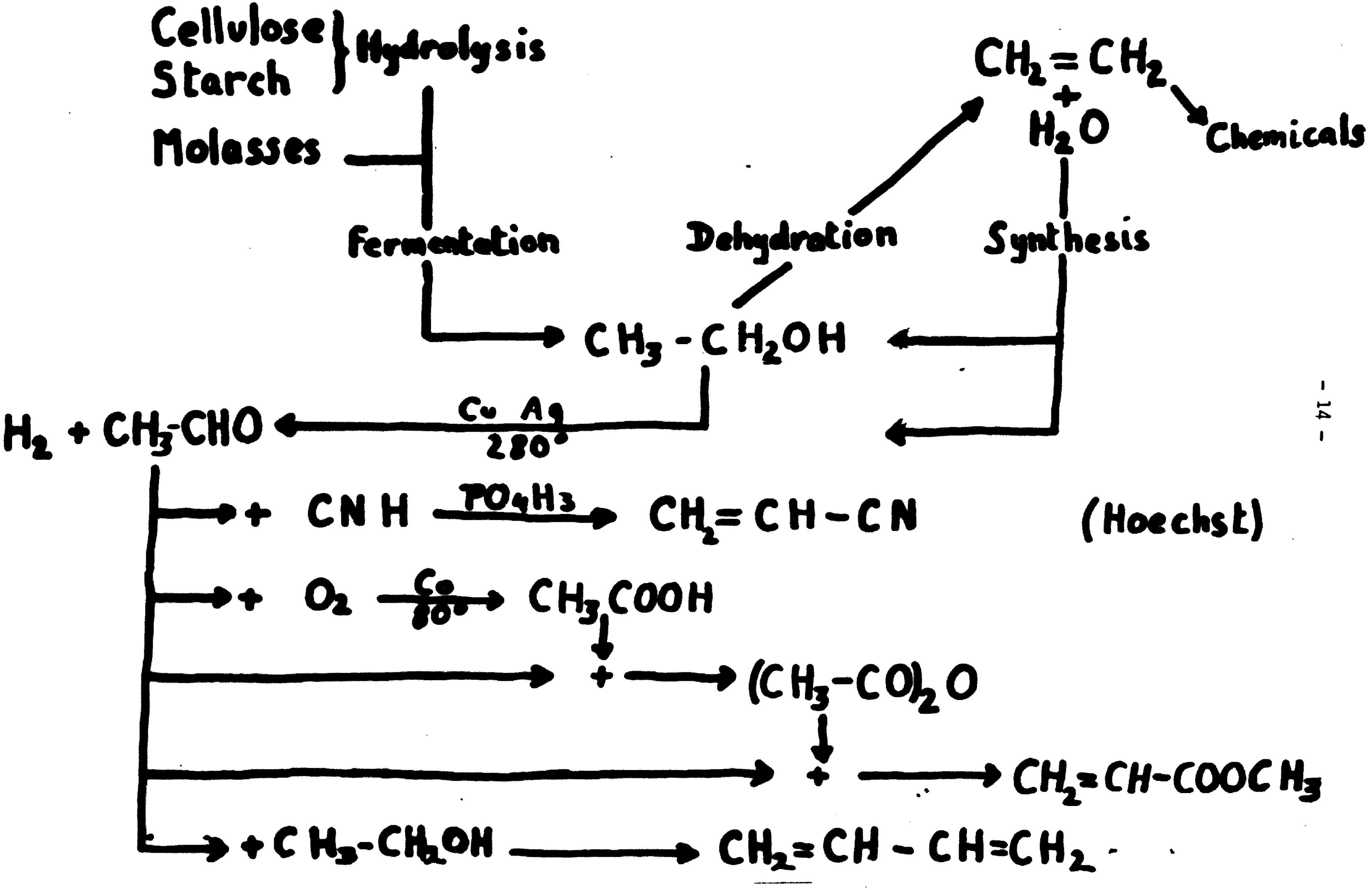


Fig. 3

Furfural Route

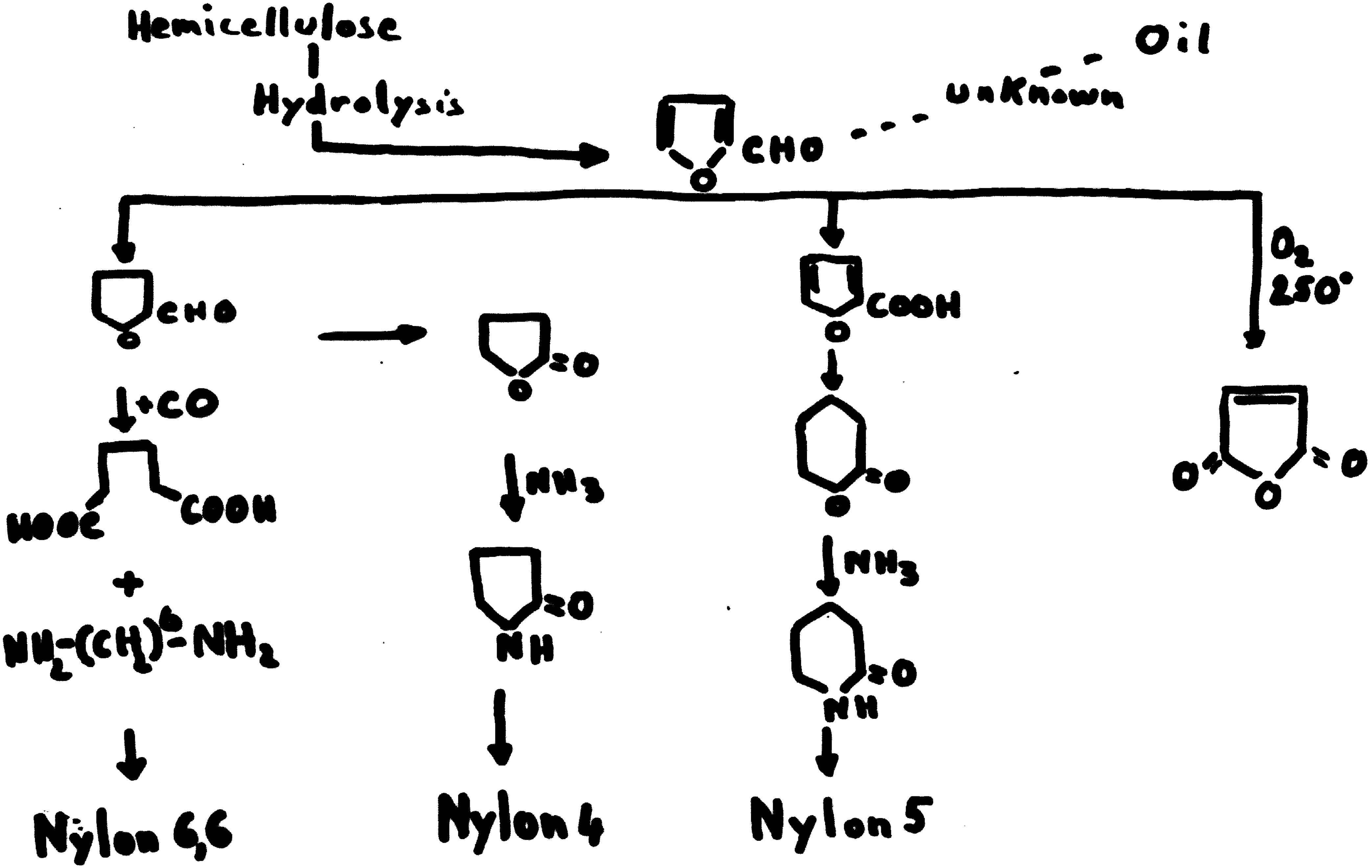
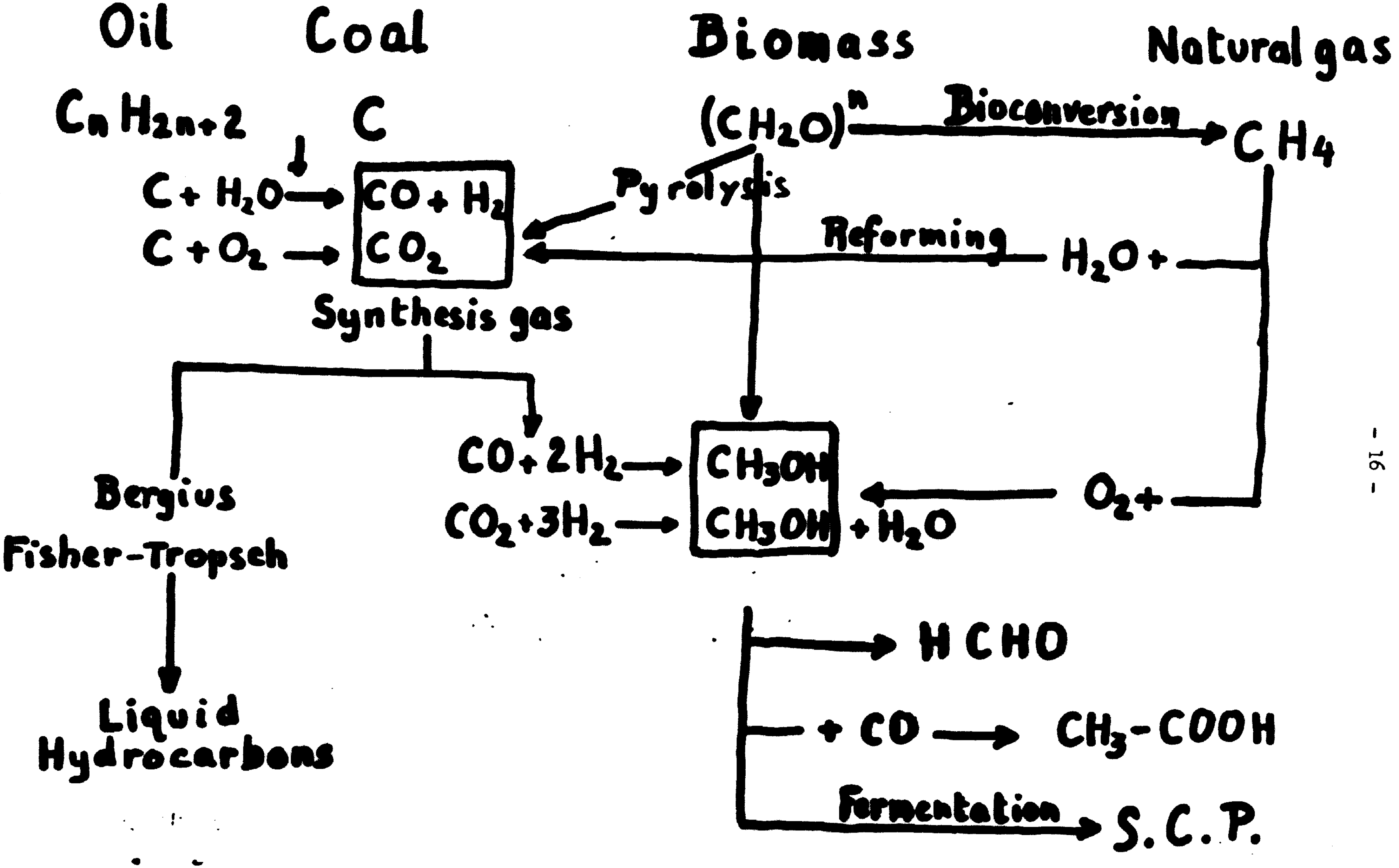


Fig. 4 Methanol Route



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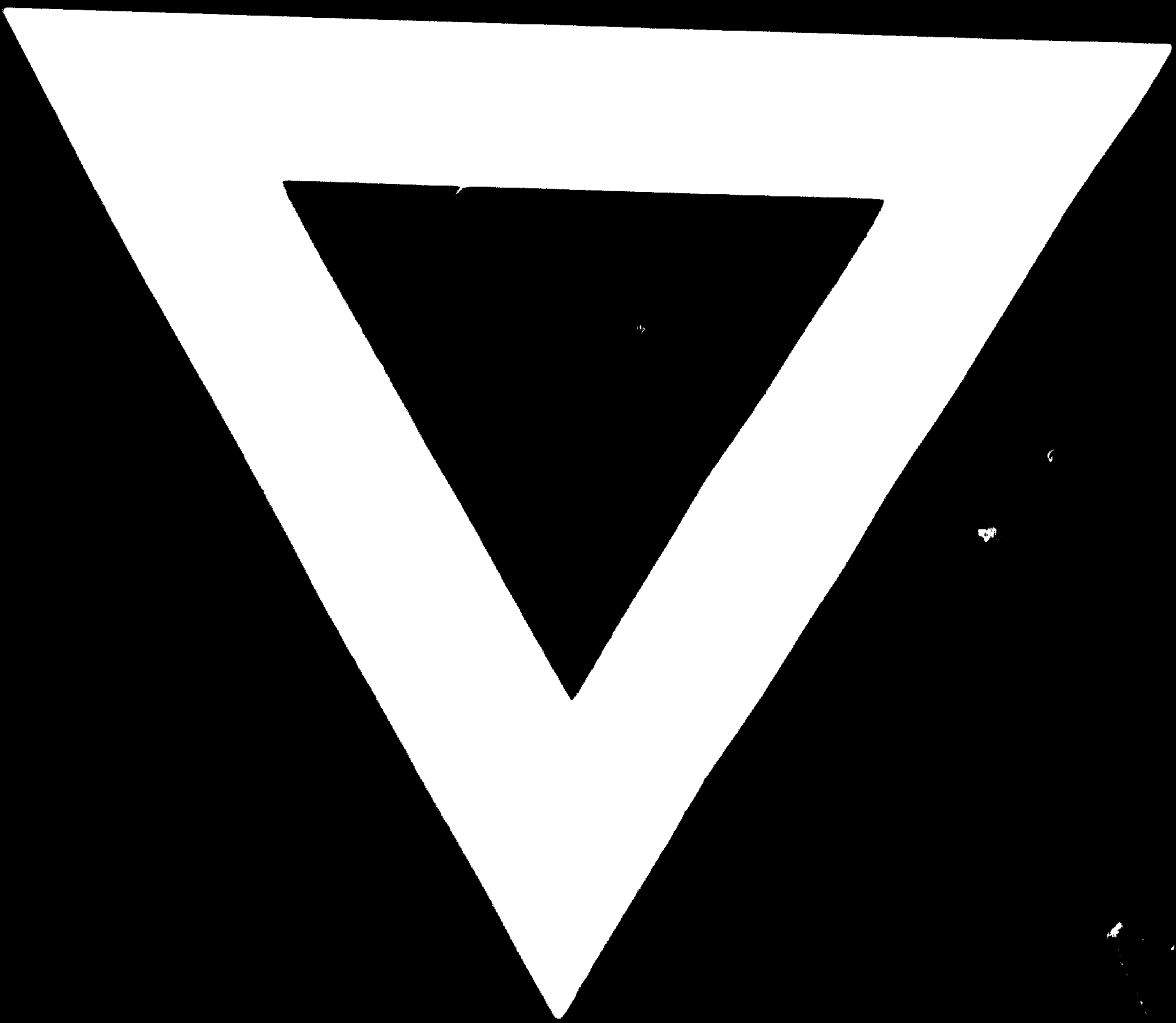

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