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MANUFACTURING GUIDE

FURFURAL[1]

by

Heinz K. Krivanec *

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* Consultant to the UNIDO Industrial Inquiry Service

[1] The following report gives the names of some of the firms which are known to manufacture and/or trade in this commodity, but the list should not be regarded as exhaustive. Inclusion in the list does not imply any recommendation by UNIDO. The views and opinions expressed in this paper are those of the consultant and do not necessarily reflect the views of the secretariat of UNIDO. This document has been reproduced without formal editing.

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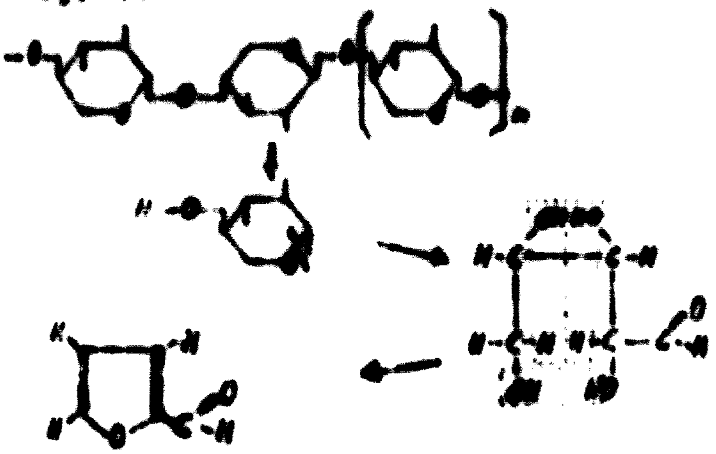
Contents

Introduction

Furfural and its derivatives have a wide range of uses which have steadily increased over the last thirty or more years but the rate of finding new uses for the chemical seems to have declined in the last few years. The demand for furfural has been met by production from a large variety of cellulosic vegetable matter. The capital outlay on plant and furfural production costs tend to be high thereby dictating plant location near to large quantities of raw materials and close proximity to large markets which can be served by bulk shipments - all to reduce transport costs.

Where these conditions exist, the exploitation of vegetable wastes can lead to the production of chemicals such as furfural, cellulose, yeasts, fertilizers etc., which have an enormous commercial value.

For the preparation of furfural from pentosan containing vegetables the latter are heated generally with dilute mineral acids at atmospheric pressure or at high pressure. The reaction is shown in fig. 1.



1. Hydrolysis
    1.1 Chain cleavage
    1.2 Ring cleavage
2. Dehydration

In the first step of the formation of furfural the pentosan chains are cleaved and seperated into the pentoses. As the reaction goes on, at high temperature and pressure, the pyranose ring is cleaved between the O-atom and the next C-atom bearing a hydroxy group and, under migration of a H-atom, a carbonyl group is formed.

In the slower second step furfural is formed by dehydration of the pentoses. The dehydration can be accelerated by varying the reaction conditions.

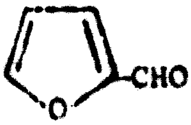
The kinetics of the formation of furfural is accompanied by decomposition reactions of the latter and a series of side reactions which diminish the theoretical yield of furfural.

Calculated on pentosan the theoretical yield is 72,7 %. As side reactions can not be eliminated, the optimal yield under laboratory conditions is around 65 % furfural. In industrial plants using agricultural wastes the yield is about 1/3 of the pentosan content in the raw material.

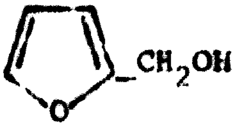
Properties and Uses

Furfural is the most important member of the family of heterocyclic compounds known as furans (1), which are characterized by a doubly unsaturated ring of four carbon atoms and one oxygen atom. Furfural is an aldehyde with the -CHO group in the 2 position, and is obtained industrially from pentosan containing agricultural residues. Related are such derivates as furfuryl alcohol and furoic acid, as well as the compounds of the tetrahydrofuran series, wherein the nuclear double bonds have been saturated with hydrogen.

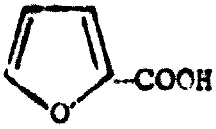
furan



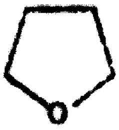
furfural



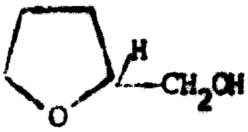
furfuryl alcohol



furoic acid



tetrahydrofuran



tetrahydrofurfuryl alcohol

In accordance with its structure, the furan nucleus is both a conjugated diene, and a vinyl ether, although the activity of these functions is diminished due to stabilization by resonance, and particularly in those furans possessing one or more electron-withdrawing substituents attached directly or vinylogously to the ring. In general, furans are more reactive and less aromatic than their benzene analogs. They undergo electrophilic substitution reactions more readily, participate in a greater variety of addition reactions, and are more susceptible to cleavage to form open-chain compounds.

Furfural (2-furaldehyde; CA) is a water-white liquid when freshly distilled, but darkens on standing in contact with air. Industrial furfural is light yellow to brown in color. It is normally handled and stored in iron or steel equipment without any special precautions, although there is a gradual darkening of color and increase in acidity and polymer formation when furfural is stored in contact with air. This autoxidation can be prevented by storing in an oxygen-free atmosphere (2). To stabilize furfural the addition of 2,5 % of water is proposed, but sodiumcarbonate, hydrochinone, brenzcatechine and tripopylamine are also efficient (A.P Dunlop, Ind.Engng.Chem. 40,204/1948/).

Physical Properties

The physical properties of furfural are given in Table 1. Figure 2 shows vapor-liquid composition for the furfural-water system. At pressures above atmospheric, the vapor-liquid equilibrium curve is pulled in toward the 45° line.

Curtis and Hatt give data for furfural-water mixtures at 72, 97 and 125 psi. Table 2 gives the mutual solubilities of furfural and water (3). The solubility in organic solvents is almost very good. Furfural is completely miscible with ethanol, ether, acetone, benzene and butylacetate. In other solvents, e.g. dekaline, furfural dissolves completely at raised temperatures but is nearly insoluble at low temperatures. In paraffines and glycerole furfurol is completely unsoluble.

Table 1. Physical Properties of Furfural

Property	Value
melting point, °C	- 36.5
boiling point, °C	161.7
density, d_4^{20}	1.1598
refractive index, n_D^{20}	1.5261
flash point, open-cup, °C	68.3
surface tension, at 30° C, dyn/cm	41.1
viscosity, cP	
25° C	1.49
38° C	1.35
54° C	1.09
99° C	0.68
heat of vaporization, at 160.6° C, kcal/g-mole	9.22
heat of cumbustion, kcal/g-mole	560.3
lower explosive limit in air, at 125° C, % by vol	2.1
coefficient of expansion, per °C	0.00110
ignition temperature, °C	393

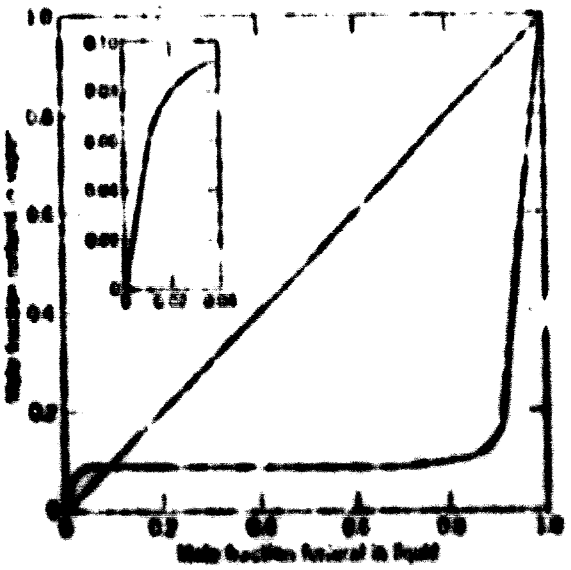
Property				Value
dielectric constant at 25° C				39.[illegible]
vapor pressure	°C	mm Hg	°C	mm Hg
	[illegible]	8	154.4	625
	92.2	[illegible]	159.0	707
	[illegible]	[illegible]	160.9	744
	131.6	310	163.8	812
	140.2	411	170.6	966

Table 2. Mutual solubility of Furfural and Water

	Furfural, wt %	
Temp, °C	Water layer	Furfural layer
10	7.9	96.1
20	8.3	95.2
30	8.8	94.2
40	9.5	93.3
50	10.4	92.4
60	11.7	91.4
70	13.2	90.3
80	14.8	88.7
90	16.6	86.5
97.9 +)	18.4	84.1

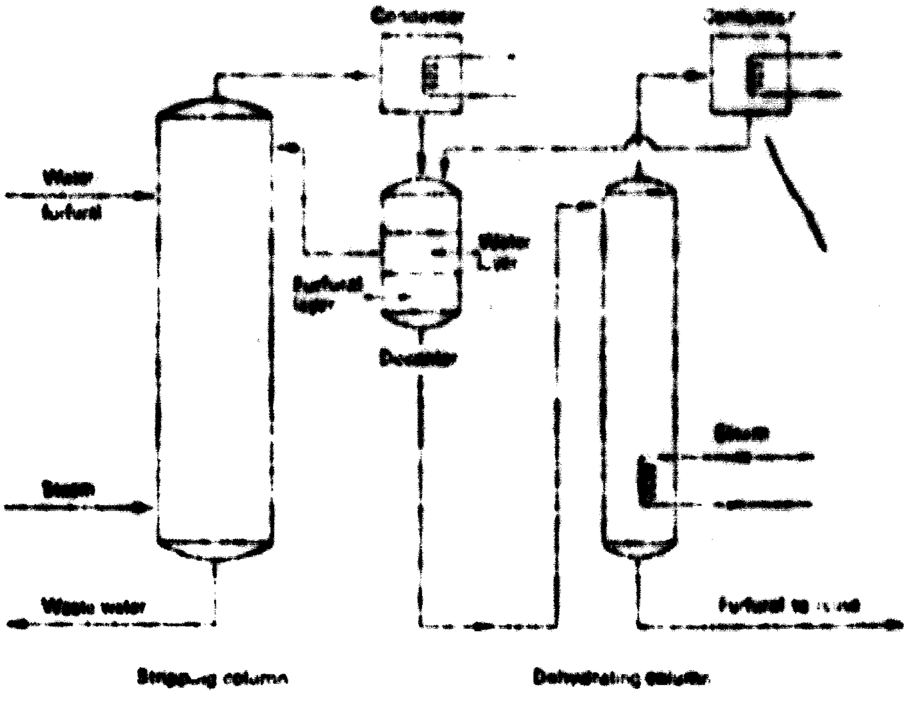
+) Boiling point at 760 mm.

Fig. 2.



Vapor-liquid composition for the furfural water system.

Fig. 3.



Furfural recovery system from aqueous solutions

Analysis

Furfural forms the usual aldehyde derivatives (phenylhydrazone mp 97° C; semicarbazone, mp 202° C) and these may be used for identification purposes. A quick qualitative test may be made by adding a few drops of a solution of aniline in glacial acetic acid to an aqueous solution of furfural (4). An intense red color develops at once if furfural is present. It is not specific for furfural, since 5-methylfurfural and 5-hydroxymethylfurfural also give a positive test.

Procedures for quantitative estimation may be divided into two groups based on (a) the aldehyde group and (b) the ring reactions. The method selected should depend on the nature of the materials present. The official method of the AOAC (new name: Association of Official Analytical Chemists) for the determination of pentosans has been most generally employed (5). This involves distillation in the presence of hydrochloric acid under carefully controlled conditions, followed by precipitation of the aldehyde with phloroglucinol. Considerable practice is required to secure duplicate results; the results obtained range from 98 to 102 % of the actual furfural content. A volumetric procedure, based on the reaction of furfural with sodium bisulfite (6), is useful in determining the aldehyde in the presence of other furan compounds, especially furfuryl alcohol. The method of Hughes and Acree is dependent upon the reaction of bromine with the furan ring under carefully controlled conditions of temperature and time (7). It gives results within 1 % of the correct value.

Many substances interfere with these furfural determinations Sometimes distillation of the furfural from an aqueous solution, as called for in the AOAC method, will eliminate the impurities.

Health and Safety Factors

Many years of practical experience, both in furfural-manufacturing plants and in users' plants, demonstrate conclusively that under ordinary plant conditions the use of furfural is not hazardous to the health of employees. Exhaustive physical examinations of workers in daily contact with furfural for as long as ten years disclosed no instance of personal injury or impairment of health. Nevertheless, ordinary common-sense precautions should be observed. As in the case of gasoline, turpentine and other well-known industrial solvents, adequate ventilation should always be provided. Furfural should not be allowed to remain in contact with the skin, as it may be a local irritant. If spilled on the body, it should be washed off with water. It will stain the skin yellow-brown if in contact with it for any considerable time. If furfural is likely to come in contact with the hands, rubber or neoprene gloves are recommended.

Due to the relatively high boiling point of furfural (161.7° C), it is difficult to build up substantial concentrations in the atmosphere. Its odor is usually sufficient warning of its presence, but chemical tests using color reactions of furfural with aniline acetate have been devised (8). Flammability of furfural is comparable to that of kerosene or no. 1 fuel oil, and may be controlled by the use of water, foam, carbon dioxide or dry chemicals.

Uses

The principal uses for furfural are for the manufacture of other furan and tetrahydrofuran compounds (including furfuryl alcohol, tetrahydrofurfuryl alcohol, furan and tetrahydrofuran); as a selective solvent for separating saturated from unsaturated compounds in petroleum lubricating oil, gas oil, and diesel fuel, as well as vegetable oil; as an ingredient in resins, especially of the phenol-aldehyde types; as a decolorizing agent for wood rosin; as a resin solvent and wetting agent in the manufacture of abrasive wheels and brake linings; and in the extractive distillation of butadiene and other C_4 hydrocarbons for the manufacture of synthetic rubber.

Chemical Intermediate. Furfural is an important chemical intermediate, used for the manufacture of a wide variety of commercial products of actual or potential industrial importance, including pyrrole and pyrrolidine, pyridine and piperidine, the essential amino acid lysine (9), methylfuran and methyltetrahydrofuran, dihydropyran and tetrahydropyran, levulinic acid, 3-valerolactone, and 5-methyl-2-pyrrolidone.

Furfural as Intermediate for Bulk Chemicals. Up to the late fifties, furfural was considered a prime candidate in the manufacture of several bulk chemicals, i.e. materials enjoying a market of more than about 20 million lbs/yr. Due to the high cost of furfural, none of these have ever materialised with the exception of hexamethylenediamine (and, of course, furfuryl alcohol and tetrahydrofurfuryl alcohol which are only accessible from furfural), one of the two components of Nylon 6.6. Its synthesis proceeded via tetrahydrofuran (as the latter has importance on its own it is being dealt with in a subsequent chapter) requiring more than 30 million lbs of furfural/yr. In 1961, Du Pont switched from furfural to butadiene which is not only a cheaper raw material but also permits to integrate production of chloroprene with that of hexamethylenediamine.

It is obvious that a valid judgment on the prospects of furfural as chemical intermediate can only be formed after detailed study of all relevant production costs. Lacking this, the general trend of the chemical industry to prefer other raw materials is certainly indicative enough to rule out furfural's use in any derivatives beyond tetrahydrofuran and those products obtained by polymerisation and/or esterification of the latter.

The poor chances of furfural as raw material for bulk chemicals seem to be due, in the last analysis, to two undesirable features, the straight chain of five carbon atoms +), and the presence of two oxygen atoms. In the first case, there was never a noticeable need for compounds containing five carbon atoms in a straight chain, in contrast to the need for units consisting of six, four or less carbon atoms. To convert furfural into the latter requires either loss of material or the addition of a one-carbon unit, both processes being more expensive than utilizing already available C_4 or C_6 feedstocks. It is also rather unlikely that a large-scale need will ever develop for C_5 straight-chain compounds, as they exhibit generally undesirable properties like low melting point and high solubility, e.g. as monomers in polymers. Further, the presence of two oxygen atoms renders furfural too expensive as oxygen atoms are either not present in bulk chemicals or, in case they

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+) This statement is not contradicted by furfural being a heterocyclic compound. Most reactions leading to bulk chemicals other than tetrahydrofuran and furfuryl alcohol proceed via ring opening.

are, are usually introduced from much cheaper sources like water or air. +)

The principles involved can be demonstrated by using an example, e.g. the synthesis of adiponitrile from either furfural or butadiene. With feedstock costs of 10 ¢ / lb and 8 ¢ / lb respectively, the four carbon atoms from furfural are more than twice as expensive as those from butadiene, not even considering yield losses, processing costs and advantages inherent in integrated manufacture of hexamethylenediamine with that of chloroprene.

The most important derivatives of furfural are (1.) furfuryl alcohol, (2.) tetrahydro furfuryl alcohol and (3.) tetrahydrofuran.

1.) Furfuryl alcohol

As the reactions of furfuryl alcohol are determined by the chemical and physical peculiarities of the furan ring system their understanding is necessary both with respect to its uses and manufacture. Due to the lower resonance energy of the furan ring in comparison to benzene, furfuryl alcohol is much more reactive than benzyl alcohol and even a hydroxy benzyl alcohol, i.e. a hydroxymethylated phenol. Although the latter can undergo self con-

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+) Raw materials containing considerable amounts of oxygen, like glucose, cellulose etc., are utilised most economically by avoiding any reactions involving loss of oxygen. It is noteworthy in this context, that the most important and fastest growing derivative of furfural is furfuryl alcohol, derived from the former without change of the basic structure.

densation and copolymerisation under mild conditions, they can be even milder in case of furfuryl alcohol. This characteristic makes it a very desirable component in applications were fast polymerisation at room temperature or slightly above is desired, e.g. in foundry resins.

The lower resonance energy of the furan ring and the presence of the ring oxygen has also undesirable consequences in that furan is susceptible to ring opening reactions which can even be caused by hydrogen. Although the conversion of furfural into furfuryl alcohol looks simple, in practice it is not. Ordinary nickel catalysts requiring low hydrogen pressure can bring about not only hydrogenation beyond furfuryl alcohol to tetrahydro furfuryl alcohol, but can also cause hydrogenolysis resulting in an economically unattractive mixture of pentanediols and pentanols. Copper chromite catalysts are much more selective but perform only under much higher hydrogen pressure necessitating expensive equipment.

Other Uses of Furfuryl Alcohol. These areas include plywood adhesives where furfuryl alcohol imparts craze resistance to urea-formaldehyde resins; chemically resistant materials (cements, mortars, bricks, linings etc.) and impregnating solutions for rendering porous materials impervious (graphite electrodes and rods, rocket nozzles and similar speciality applications). Small amounts of furfuryl alcohol are also used in the abrasives and textile industry. In the U.S.A., the total consumption of furfuryl alcohol for such applications is probably between 5 and 10 million lbs/yr, in other countries correspondingly less, e.g. in the Federal Republic of Germany consumption is estimated at being not much in excess of 2 million lbs/yr.

The markets are characterized by close supplier-customer relationships with many small manufacturers selling their specialised products. In some areas growth has been quite brisk, the sales volume having doubled within five to six years. In general, the markets are somewhat difficult to analyse and the growth rate may be about 10 % / yr.

2.) <u>Tetrahydro furfuryl alcohol</u>

As Quaker Oats is the only producer of this material, even approximate figures on consumption and market trends cannot be obtained. It is used as specialty plasticiser and carrier for stabilisers of PVC and as solvent of various polymers. It is highly unlikely that world consumption exceeds 7 - 8 million lbs/yr.

3.) <u>Tetrahydrofuran</u>

Commercially important uses are:

a) As solvent for PVC (polyvinyl chloride), PVDC (polyvinylidene chloride) and its copolymers and, to a lesser extent, in certain GRIGNARD reactions. Growth in these areas was good and is expected to continue, (i.e. in topcoating automobile upholstery, specialty adhesives, film coatings and castings, printing inks etc.).

b) its polymerisation and/or esterification to stretch fibers and other polyurethans. Both of these uses are also growing very well.[+)]

From the beginning of the commercial THF manufacture two different processes were employed. While Du Pont used to, and Quaker Oats still does, use furfural as starting material (via decarbonylation to furan and subsequent hydrogenation), BASF's route is based on acetylene and formaldehyde. In 1968, Du Pont switched from furfural to the West German process or some modification of it, thus turning from a furfural consumer to a supplier of THF. Du Pont's move was allegedly prompted by steadily increasing furfural prices and the uncertain supply situation for furfural during the Dominican crisis.

[+)] Precise figures are not available as there are only two producers of THF in the U.S.A. and one in Western Europe. It has been rumored that total U.S.A. capacity is around 35 million lbs/yr, in Germany 22 million lbs/yr and in Japan 8 million lbs/yr.

Furfural as Intermediate for Chemical Specialties. As a raw material for bulk chemicals, i.e. materials with a sales volume of more than 20 million lbs/yr. furfural has, as has been shown, no or at best very risky chances if those compounds contain four carbon atoms or less. In these cases raw material costs, economy of scale and certainty of supply weigh too heavily in favour of petroleum feedstocks. +) Further, it should not be overlooked that much industrial chemical research is based on the large scale availability of certain raw materials seeking a profitable outlet which situation tends to reduce even more the chances of furfural as chemical intermediate.

The outlook is somewhat better for specialty chemicals with a sales volume of up to about 10 million lbs. Unfortunately, there are too many products in this field to conduct a thorough survey. The picture becomes even more inscrutable as the products concerned are often proprietary and volume figures are almost impossible to obtain. A study of the patent literature is equally unavailing as no information can be gained on products actually manufactured and the processes or raw materials actually used. Good personal contacts may here and there permit a more penetrating look, but this will remain an exception. Finally, forecasting consumption

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+) The events since the last months of 1973 may considerably change the situation on the petroleum market in the future.

based on price relationships between furfural and competitive raw materials is in many cases not feasible.

The group of nitrofurans comprises a number of commercially accepted antimicrobials of a surprisingly wide activity spectrum. The most potent compounds are used as bactericides and fungicides, among which the so-called nitrofurazone is probably known best. All nitrofurans have one structural feature in common, as they are derivatives of 5-nitrofurfural. Norwich Pharmacal holds many of the basic patents in this field and probably enjoys the lion's share of the market the size and growth rate of which is not known. It appears reasonable to assume a market in the area of a few hundred thousand lbs/yr.

Another product is lysine, an essential amino acid which most plant proteins contain but in insufficient amounts. It is argued by many nutrition specialists that undernourishment in various countries can be eliminated by supplementing the regular diet with lysine. Furfural was again proposed as one of the potential starting materials, but it should be mentioned that at present lysine manufacture is based on microbiological processes.

Further, a very potent analogue of the insecticidal pyrethrum class can be based on furfural. This new process is to be commercialised soon. The amounts needed could be very large but detailed information is as yet not available.

Another potential application of furfural is in the manufacture of *levulinic acid*, via furfuryl alcohol. Levulinic acid is the starting material for the manufacture of diphenolic acid, a valuable ingredient in polishes and other specialty coatings. Again, the commercial manufacture by Crown-Zellerbach by-passes furfural and is based on pulp or cellulose, respectively.

Finally, *dihydropyran* is another chemical derivative of furfural, made via furfural and tetrahydro furfuryl alcohol. Its proposed use in lysine synthesis has already been mentioned.

Furfural as Selective Solvent in the Refining of Oils. Furfural is one of the most widely used solvents in the refining of lubricating oils to increase the stability under operating conditions and to improve the viscosity-temperature relationship (10). Mineral oils processed range from diesel fuel to heavy lubricating-oil stocks of over 200 SUs viscosity at 210° F. The extracted oil output of individual plants varies from 60 to 10,000 bbl per day, while the stocks processed include naphthenic and paraffinic distillates and residues.

The furfural refining process, developed industrially by the Texas Company, involves extraction of raw lubricating stock with furfural at temperatures generally below 250° F, to yield a refined oil and an extract (11). The undesirable aromatic and olefinic components of the oil are selectively dissolved by the furfural and thereby separated from the desirable paraffinic and naphthenic components. Oil enters near the bottom of a countercurrent extraction column and furfural is applied at a point near the top. The extract is removed from the bottom of the column with the bulk of the furfural. The furfural losses are generally 0.02 % or less per cycle.

Natural glyceride (fatty) oils may be separated into two or more different fractions by the use of furfural as a solvent in an operation similar to that used for refining mineral oils (12). Although the process has been used chiefly to make separations based on degree of unsaturation within a glyceride mixture, it may also be used to fractionate fatty acids, concentrate valuable minor ingredients of oils, or separate compounds of different molecular weight.

<u>Furfural as Decolorizing Agent for Wood Rosin.</u> The Hercules Powder Company developed the use of furfural to remove color bodies frum crude FF grade wood rosin to produce a light-colored product capable of competing with gum rosin, which is used in the soap, varnish, and paper industries. After removal by fractional steam distillation of most of the color bodies, which react with alkali to produce red products, are extracted with furfural from a solution of the crude rosin in warm gasoline. Since furfural and gasoline

are almost entirely immiscible at low temperatures, a furfural-gasoline-rosin solution separates into two layers on cooling. A light-colored rosin is obtained on evaporation of the gasoline layer and the furfural is recovered by distillation of the other layer (13).

By adjusting the operating conditions it is possible to produce rosin to conform to any grade on the American scale up to X grade.

Furfural as Reactive Solvent in the Manufacture of Resinoid-Bonded Grinding Wheels. For many years resin-bonded abrasive wheels have been made with furfural. In the manufacture of cold-molded grinding wheels, the abrasive grain is wetted with furfural, or a solvent mixture containing furfural, followed by addition of the desired amount of pulverized phenolic resin. (14)

Furfural as Extractant for Butadiene. Furfural is used as an extractive distillation medium in one of the principal processes for the manufacture of butadiene from petroleum, as developed by Phillips Petroleum Company. The furfural losses are extremely small (0.01 - 0.02 % of the circulation rate). Hydrocarbons with four carbon atoms, such as n-butane, isobutane, 1-butene, 2-butene, and butadiene, have similar boiling points but widely different solubility characteristics. When distillation of the mixtures is carried out in the presence of furfural, the relative volatility of the several C_4 hydrocarbons is altered sufficiently to effect ready separation (15).

Furanpolymers. Furfural and its commercially important derivatives furfuryl alcohol and tetrahydrofuran are used to make polymers with widely different properties. In the last decade several striking new uses for the polymers, for example, in spandex fibers, impervious nuclear graphite, and "hot-box" or "no-bake" foundry binders, have focussed attention on these materials.

Special consideration should be given to (1) Polymers from furfural and (2) Polymers from furfuryl alcohol. .

1.) Polymers from Furfural

a) **Furfural-Phenol Resins.** The most important polymers of furfural are based on its ability to react with phenol to form thermosetting resins. Although such polymers are commonly used in place of, or blended with, phenol-formaldehyde resins, there are several important differences in the preparative techniques. For example, the commonly used phenol-formaldehyde novolacs are formed by reacting formaldehyde with a slight molar excess of phenol in the presence of an acid catalyst. Similar conditions employed to polymerize furfural and phenol give gels, unless a large excess of phenol is present to inhibit acid degradation of the furfural (16). The furfural-phenol resin preparation is usually carried out using alkaline catalysts, typically potassium carbonate or sodium hydroxide. Resins of the novolac type consume the majority of the furfural used by the phenolic resin industry. They are characterized primarily by long flow times for a given curing speed, and are widely used in molding compounds.

b) Furfural-Acetone Resins. Furfural reacts with ketones to form polymeric materials that have been of interest especially in the Soviet Union. The furfural-acetone resins have been used to form resin-aggregate mixtures which have been termed "organic concretes". These are reported to have many excellent properties and to be used in the Soviet Union, yet there has been virtually no commercial use of such resins in other countries despite these favorable reviews.

2.) Polymers from Furfuryl Alcohol

Furfural is hydrogenated to furfuryl alcohol, which is a much more versatile polymer precursor. Its properties are listed in Table 3.

Table 3. Properties of Furfuryl Alcohol

empirical formula.	$C_5H_6O_2$
molecular weight	98.1
boiling point (760 mm), °C	170
refractive index, n_D^{20}	1.4868
density, 20/4° C	1.1285

The alcohol is a mobile liquid which resinifies readily in the presence of acids. In addition to the normal reactions of a primary alcohol, furfuryl alcohol reacts via the ring hydrogen atoms, and by ring cleavage. Accordingly, commercial polymers of furfuryl alcohol are complex mixtures. Usually they are based on the reaction of the alcohol not only with itself but also with coreactants such as formaldehyde, urea, and sometimes phenol. The common method of making furfuryl alcohol polymers involves reaction in the presence of an acid catalyst, usually with heat, until the desired degree of polymerization is achieved. Soluble polymers, varying from low-viscosity liquids to brittle fusible solids, may be obtained by altering reaction conditions (17).

Furfuryl Alcohol in Foundry Resins. During the last few years furfuryl alcohol based foundry resins have shown an extraordinary growth rate, the demand having doubled repeatedly within spans of two to five years in the U.S.A., United Kingdom and the Federal Republic of Germany. This was due to two factors, the growth of the foundry industry and, more important, a change in technology of making cores and moulds. The two main processes in which furfuryl alcohol based resins are used are the "hot-box" and the "no-bake" process. While the former is employed in the production of items of small size manufactured in large number, e.g. automotive parts, the latter finds its typical application in the manufacture of large items, e.g. ship propellers etc. The furfuryl alcohol content in the "no-bake" resin is, on average, 60 - 65 % and 40 - 45 % in the "hot-box" resins. There is no agreement in which ratio the two resins are being produced but the present annual consumption of furfuryl alcohol for all foundry purposes in the U.S.A. amounts to 45 - 50 million lbs/yr, in the eral Republic of Germany to 15 - 16 million lbs/yr and in the United Kingdom, despite its bigger foundry industry, to 12 - 13 million lbs/yr. The furfuryl alcohol consumption figures for this application in the other European countries could not be obtained but may be assumed to be somewhat smaller than those for the United Kingdom and the Federal Republic of Germany.

Practically everybody in the foundry resin business is convinced that furfuryl alcohol will be consumed in increasing amounts. The annual growth rates for the U.S.A. and the United Kingdom are estimated to be 12 - 13 % and for the Federal Republic of Germany 15 - 18 %, these rates to continue for the next five to eight years. These optimistic forecasts are based on the following:

a) The change-over to new technology in mould and core making will continue.

b) Foundries will continue to expand.

c) Furfuryl alcohol resins have certain technological and economic advantages over competitive materials, e.g. phenolics and polyurethans (alkyd-isocyanate condensations products).

Of these, the latter are generally not considered a serious threat to furfuryl alcohol as they are more expensive and show less hot-strength, a serious disadvantage in steel casting. However, it is very difficult to compare the relative advantages and disadvantages of furfuryl alcohol resins and phenolics, i.e. phenol-formaldehyde-urea condensation products. Obviously, phenolics are less expensive and have more odour; they give rise to cleaner castings and are also less brittle and show higher cold strength, both properties being important for thin sections. But phenolics cure more slowly, are less stable, especially at room temperature and do not cure well in thick sections. As a result, phenolics are not being used in the "no-bake" process which is the domain of furfuryl alcohol based resins.

In addition to the advantages just mentioned, furfuryl alcohol resins permit more flexible foundry operations in that they can be used equally well with warm or cold sand and at variable curing rates; they also permit sand re-use. Finally, their decisive advantage seems to be that they do not cause any pollution as do phenolics. This advantage was stressed by Wes German manufacturers who believe that consumption of furfuryl alcohol in the British and American foundry industries will go up sharply as soon as more stringent anti-pollution laws are passed. At present, the used sand is discarded without too much concern for rain or ground water leaching out large amounts of unreacted phenol, with subsequent pollution of rivers. As furfuryl alcohol polymerises completely under all curing conditions encountered in foundry practice, it cannot give rise to similar situations. (See references 18, 19, 20, 21, 22, 23, 24, 25 and 26).

Sources

Furfural is obtained from the pentosan in cellulosic vegetable matter, but only certain materials have a sufficiently high pentosan content to make them viable as a raw material for furfural production.

Vegetables, annual or perennial plants, are principally composed of lignin, cellulose, and hemicellulose. Many constitute agricultural or industrial by-products, these latter of industries which use them as raw materials.

Their inherent characteristics often render them useful for the production of various substances: cellulose or semi-cellulose, sugars for yeasts, furfural, shredpanels etc.

Up until now, however, the drasticity of the treatments necessary or not directed toward multiple productions, has meant only the partial utilization of these products. An exception is the production of cellulose bisulphate, which make partial use of the sugars formed during the boiling treatment, sugars which are then transformed into Torula yeast.

Even in this case, it is impossible to separate the two treatments, to a technical and economic advantage, partially or totally removing in the beginning those fractions which are not useful or which are damaging to the production of cellulose or semi-cellulose, transforming these fractions in sugars destined for various other uses. This process is decisive for vegetables having a high pith content (corn cobs, bagasse, etc.)

Through a hydrolytic treatment, controlled so as not to alter the characteristics of the residual fibrous mass, it is possible to achieve a complete utilization of the vegetable, separating the various fractions destined for successive transformations. The successive treatment also benefits through this technology, often with notable advantages in return and, principally, with a total utilization of the vegetable constituents, constituents which can provide:

a) <u>for the soluble fraction of the hydrolysis</u>

- a total utilization of the reducing sugars having five or six carbon atoms, directing them as mentioned, to the production of yeast;
- a selective utilization of the sugary fraction having five and six carbon atoms respectively for the production of furfural and then of yeast.

  This possibility is related primarily to those vegetables which contain a high percentage of pentosans and thus render the production of furfural more economical and rational.

b) <u>for the fibrous fraction, insoluble</u>

- a utilization for the production of cellulose or semicellulose;

- a utilization for the production of shredpanels;
- a utilization for the production of a fertilizer of the humus type.

In the case of the soluble sugary fraction, the successive change to furfural, as far as the return is concerned, profits considerably from the separation from the lignin, which remains in the fibrous mass and which in the opposite case chemically fixes the furfural forming resins; it also profits from the more rapid elimination from the acidic production solution, since it is liquid, thus avoiding polymerization reactions.

In the production of bidistillate furfural, working directly on the woody mass, the returns center around 50 % of the theoretically possible quantity; for the production from solution through hydrolysis, the returns vary around 80 % (Simafer S.P.A.).

In the case of the fibrous fraction the successive treatments are thus benefitted:

- the production of semi-cellulose and cellulose requires fewer boiling reagents; the product obtained demonstrates a better driping quality, a characteristic valued in the manufacture of paper.
- the production of shredpanels requires a lower consumption of adhesive resins and permits a more uniform distribution of the same.

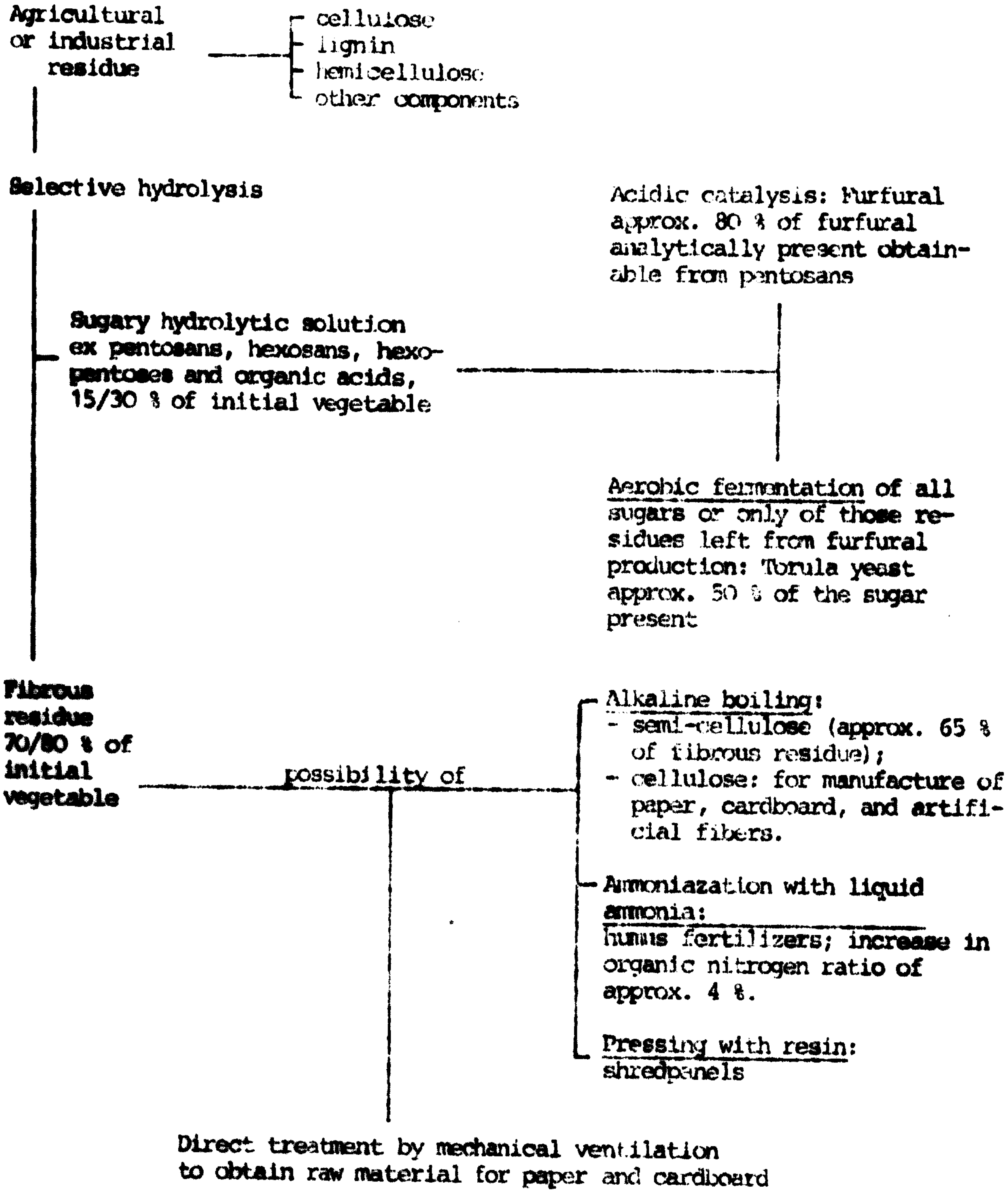
- the production of humus fertilizer permits a greater nitrogen fixation in the form of amino groups, through the opening of bonds between lignin and cellulose, an opening obtained by means of hydrolysis.

Recent studies (Simafer S.P.A.) for improving the production of furfural in the plants which operate in the solid phase have led to a partial recovery of the residual hexosic sugars and to an improvement in the characteristic of the residual reaction mass, rendering it more suitable for the ammonizing process.

In conclusion: the selective hydrolysis treatment carried out prior to the normal treatments, both for obtaining raw materials for the paper and cardboard industry as well as for obtaining furfural, yeasts, shredpanels, and humus fertilisers, leads to a more complete utilization of the vegetable components and improves the successive manufacturing phases.

The possibilities obtainable from vegetable wastes through selective hydrolysis are shown in Table 4.

Table 4.



Agricultural or industrial residue

- cellulose
- lignin
- hemicellulose
- other components

Selective hydrolysis

Sugary hydrolytic solution ex pentosans, hexosans, hexopentoses and organic acids, 15/30 % of initial vegetable

Acidic catalysis: Furfural approx. 80 % of furfural analytically present obtainable from pentosans

Aerobic fermentation of all sugars or only of those residues left from furfural production: Torula yeast approx. 50 % of the sugar present

Fibrous residue 70/80 % of initial vegetable

possibility of

Alkaline boiling:
- semi-cellulose (approx. 65 % of fibrous residue);
- cellulose: for manufacture of paper, cardboard, and artificial fibers.

Ammoniazation with liquid ammonia:
humus fertilizers; increase in organic nitrogen ratio of approx. 4 %.

Pressing with resin:
shredpanels

Direct treatment by mechanical ventilation to obtain raw material for paper and cardboard

As mentioned above, Furfural is usually formed from pentosans by hydrolysis and condensation and therefore can be commercially produced from most pentosan containing raw materials, such as certain annual plants and hard-woods. Quite a lot of raw materials are already known to be utilized for this special purpose, as shown in Table 5.

Table 5

Raw Material	% by weight of pentosans
acacia wood (after tannin extraction)	20
bagasse	25 - 27
bagasse pith	25
birch wood (after tannin extraction)	25
chestnut husks	11
chestnut wood (after tannin extraction)	16
corn cobs (stoned)	30 - 32
corn husks	30 - 33
corn stalks	24
cotton husks	23 - 28
flax stalks	16 - 19
hemp husks	15
oak wood (after tannin extraction)	20 - 21
oat husks	40
peanut husks	14 - 17
rice husks	16 - 18
sansa	22 - 25
sunflower husks	30 - 33
wheat chaff	18

The above data are average values varying to a certain extent with the local conditions for the different raw materials. In general, the furfural yield amounts to about 1/3 of the pentosan content.

In conventional processes the transformation of the pentosans via pentoses into furfural is carried through either by heating the raw materials with H_2SO_4 at increased pressure or by using HCl at lower temperature and normal pressure. Another process which is known is working with phosphoric acid.

Recent developments are directed to continuous processes in vertically arranged reaction vessels at moderate temperature and pressure using only little amount of SO_2 acetic acid as catalyst, if any.

Manufacture

General Remarks

The market for furfural and furfural-based chemicals (furan chemicals) is dependent upon the activities of one major producer (Quaker Oats Ltd). Therefore, to understand the furan chemicals market it is relevant to make some reference to production aspects (without going into the actual technology of furfural production) since these explain, in part at least, the advantages that the leading company has in this industry.

a) **Capital Investment** : The investment cost of a furfural plant per unit return from sales is relatively high, particularly for a small plant. This is due to the fact that the process involves a number of unit operations requiring a large number of different kinds of equipment and partly to the fact that it is necessary to provide facilities for processing solid, liquid and gaseous waste products.

b) **Plant Size** : In order to get the per unit cost of the plant down to a reasonable level, it is necessary to build large plants. The economies of scale obtained from larger plant are illustrated by the following figures quoted by one chemical manufacturing company: in Africa a 2,000 tons per annum capacity plant would cost about

US $ 900,000, one of 3,000 tons US $ 1.100,000 and one of 5,000 tons US $ 1.700,000. However, the minimum economic size of plant, as quoted by different companies, ranges from 2,000 tons capacity a year to about 10,000 tons, and for the latter capacity the cost might be around US $ 2,3 million.

c) Plant Location : The yield of furfural per ton of raw material is so low that the price which can be paid for raw material is little more than the cost of collecting and handling. Dispersed location of agricultural waste products would add a collecting cost item which may be prohibitive for a profitable level of production costs, and an annual output of 5,000 tons of furfural would require over 50,000 tons of raw material. Quaker Oats Ltd. in the U.S.A. has a very real advantage in that their raw material is practically a zero cost input because furfural production utilizes the waste products of the main agricultural processing activity; thus raw material collecting costs are primarily borne by this major process. It is also a considerable advantage to have a steady supply of raw materials over the year since the furfural content of the agricultural waste material decreases unless storage is well-controlled. Distribution costs of the final product should be kept down to a minimum by bulk shipments, (Quaker Oats Ltd. considered units of 5,000 tons each to be the most viable), the break-of-bulk operation into drums being performed in the consuming areas.

Description of the Different Processes

In the following chapter we describe the different processes and plants in alphabetic order.

a) ESCHER WYSS GmbH Ravensburg

The plant for the continuous production of furfural is working on the following principle:
The raw material is fed with a transporting device (e.g. belt conveyor, bucket elevator, pneumatic conveying system with cyclones and a dust suction plant) into the impregnation part.

This is either an impregnation tank or a system of screw conveyors.

In case 1. (Alternative 1) all granular materials with high bulk weight such as corn cobs, rice husks, wood chips etc are fed through a worm conveyor (see flow sheet 1.1, page 4[illegible]) into the impregnation apparatus (1.1). The overflow will be returned by means of a transporting device into the raw material storage bin. In the impregnation apparatus, the raw material will be pretreated by adding water or vinasse containing the catalyst (e.g. SO_2 or acetic acid) and preheated with secondary steam from the secondary steam generating plant (group 2). The pretreated raw material is transported with a controlled worm conveyor which is arranged at the bottom of the impregnation apparatus (1.1), into the rotary valve funnel of the digester filling system (1.2). Then it is fed by the rotary valve (1.2) into the digester (1.3) which is operating under pressure and temperature.

In case 2. (Alternative 2), fibrous, straw-like raw materials with low bulk weight such as corn stalks, bagasse as well as all kinds of straw and stalks are pretreated in a system of screw conveyors (1.1) where it is impregnated with the catalyst and preheated with secondary steam. The impregnated raw material is fed into the digester by the digester filling system (1.2) which is in this case a press-screw. The impregnation liquid drained in the press-screw flows back into the catalyzer additional equipment (1.9), from where it returns into the impregnation part by means of a pump. The raw material moves slowly to the digester bottom where it is discharged by a digester discharge device (1.4) into the blow tank with discharge device (1.5). In this blow tank (1.5), the furfural containing flash vapors is separated under atmospheric pressure from the residue which later is discharged through a pocket wheel, for example. The flash vapor is condensed in a flash vapor condenser (1.6.) and flows either into the catalyzer additional equipment (1.9) or if it contains a greater amount of furfural, into the distilling plant.

The primary steam, for heating the raw material up to 190° C and extracting the formed furfural, enters the digester (1.3) in the bottom and is continuously extracted in the top. The furfural loaded steam is cleaned in a separator for solid matters (1.7) from raw material having been carried along. Any remaining solid matters will be separated by sieve filters (1.8).

In a condensing and secondary steam generating plant (group 2.), the furfural containing primary steam (under simultaneous generating of secondary steam for heating the distilling columns) is condensed, cooled and deaerated. This plant is laid out for 200 % capacity - 100 % as reserve.

The primary steam condensing in the tubular condenser (2.1.) flashes in the condensate cooler (2.3.) and is cooled down to about 60° C. The furfural containing condensate is deaerated in the air separator (2.4.) and collected in the furfural condensate collecting tank (3.1.).

The feed water from the feed water station (2.6.) is heated up in the condensate cooler (2.3.) and evaporated in the tubular condenser (2.1.). The generated secondary steam will be separated from the feed water having been carried along in the fluid separator (2.2.).

Air and non-condensable gases as well as vapors are cooled or condensed in a vent cooler (2.5.).

From the furfural condensate collecting tank (3.1.) which at the same time serves as buffer tank, the 5 to 7 % furfural containing raw condensate is conveyed to the distilling column (3.5.) by means of feeding pump (3.2.) - two pumps, one as a spare. In this way the raw condensate is preheated to about 95° C in the furfural condensate preheater (3.3.) by means of the hot vinasse extracted from the lower part of the distilling column (3.5.) over the vinasse pump (3.4.).

The vinasse is simultaneously cooled down to about 70° C and will either be gathered in a tank of the catalyser additional equipment (1.9.) or fed in the canalization. The heating of the distilling column (3.5.) is effected indirectly in the column heater (3.6.) by secondary steam of about 3kg/cm^2 (gauge).

The vapors from the distilling column (3.5.) are flowing into the methanol distilling column (3.7.). From the dephlegmator (reflux condenser) (3.8.), a methanol and water mixture with about 84 % methanol is withdrawn and cooled down to approximately 25 - 30 ° C in the methanol cooler (3.9.). The methanol collecting tank (3.10.) serves only as intermediate tank for crude methanol from which the same is conveyed to its further utilization.

The sump of the methanol distilling column (3.7.) is designed as separator vessel. The overflow - a water and furfural mixture - returns into the distilling column (3.5.) as reflux. The bottom discharge is an azeotropic mixture of furfural and water with about 84 % furfural. This azeotrope which left the sump at a temperature of about 97° C, is cooled down in the azeotrope cooler (3.11.) to 25° C.

In a second furfural separating vessel (3.12.), further separation of the furfural and water mixture is carried out. The overflow with 8,5 % furfural is partly used for solution of the soda in the soda solution tank (3.13.), the rest returns as reflux either in the distilling column (3.5.) or furfural condensate collecting tank (3.1.). The bottom discharge of the furfural separating vessel with 94,5 % furfural is flowing continuously into the neutralization tank where it is mixed with the soda solution by means of a circulation pump (3.15.). In the container for neutralized furfural (3.16.) the neutralized furfural water solution is collected and conveyed into the dehydrating and purifying column (3.18.) by means of a feeding pump (3.17.).

This column is operating under vacuum, which is maintained by air suction pumps (3.20.) - two pumps, one as a spare.

The heating of this column (3.18.) takes place indirectly by secondary steam of 3 kg/cm² (gauge) over a heat exchanger in the bottom of the column. The impurities precipitated in the dephlegmator (reflux condenser) (3.19.) - water, acetone and other easily volatile substances - are partly recirculated into the column as reflux, sucked off by the air suction pump (3.20.) together with the non-condensable substances or they return into the furfural condensate collecting tank (3.1.).

The 99,5 % furfural, extracted from the purifying column (3.18.), is cooled in the pure furfural cooler (3.21.) and collected in the pure furfural collecting tank (3.22.). The furfural can be conveyed either into another tank or to a filling station.

The residue from the sump of the purifying column (3.18.) is extracted from time to time into the residue collecting tank (3.24.).

Thermal Recovery. It is possible to regain the greatest part of the thermal energy used in the reactions, as secondary steam (low pressure steam) and hot water. The low pressure steam is produced in the seconoary steam generator (group 2.); secondary steam condensate, resulting in the circuit, serves as feed water which can be reused.

The secondary steam not consumed to heat the column apparatus can be used on the other hand as hot water in order to gain the best thermal economy.

Production of Acid . Sometimes it is possible to produce acid, which is dependent on the raw material used. For this purpose an apparatus can be connected additionally to this plant.

On page 44 of this report, you can find an information sheet showing an example for calculating the operating costs of a continuous furfural plant working according to the ESCHER WYSS system.

For further information please contact:

ESCHER WYSS GmbH
798, Ravensburg / Württ. Federal Republic of Germany

Information Sheet 1/69 of Escher Wyss GmbH Ravensburg

Example for calculating the operating costs of a continuous Furfural Plant working according to the ESCHER WYSS System.

As the costs for raw material, chemicals, steam, power etc. are different in each country, this calculation has informative character only and must be drawn up separately by each company, depending on the special conditions prevailing there.

Cost Occurence		Price per Unit	Required amount at yield (%) of	Costs at yield (%) of	Remarks
			10 9 8 7 6 5	10 9 8 7 6 5	
I Raw material	(pentosan content in %)	DM/t b.d.	t b.d./t furfural		
II Chemicals					
SO_2-liquid (catalyst)			abt. 1%/t b.d. raw material (kg)		
Na_2CO_3 (neutralization)			abt. 0.4%/t b.d. raw material (kg)		
III Steam (15kg/cm^2 gauge pressure)					
IV Water (20° max.)					
V Power					
VI Wages and Overheads					
VII Maintenance and repairs		DM/t			
VIII Operating costs without amortization and interest					
IX Amortization and interest			yearly production (t) 300 days		
costs f. equipm.					
interest rate:					
duration					
costs for buildings:					
interest rate		yearly amortization			
duration:					
X Costs per ton of furfural at various yields and raw materials DM					
XI By-products			quantity in t/t furfural abt.	returns in DM/t furfural	
Hydrolysis waste (4500 kcal/kg)					
calculated as oil equivalent					
Methanol					
Acetone					
XII Returns per t of furfural by by-products					

Information Sheet 1/68 of Escher Wyss GmbH Ravensburg

Example for calculating the operating costs of a continuous Furfural Plant working according to the ESCHER WYSS System.

As the costs for raw material, chemicals, steam, power etc are different in each country, this calculation has informative character only and must be drawn up separately by each company, depending on the special conditions prevailing there.

Cost Occurence	(pentosan content in %)	Price per Unit	Required amount at yield (%) of 10	9	8	7	6	5	Costs at yield (%) of 10	9	8	7	6	5
I Raw material		DM/t b.d.	t b.d./t furfural											
Corn cobs (stoned)	30	10.—	10,0						100.—					
Cotton husks	27	10 —		11,1						111.—				
Bagasse pith	25	40 —			12,5						500.—			
Oak wood (extracted)	21	40 —				14,3						572.—		
Rice husks	18	40 —					16,7						167.—	
Chestnut wood (extracted)	15	40 —						20,0						800 —
II Chemicals			abt. 1%/t b.d. raw material (kg)											
SO$_2$-liquid (catalyst)		50.— DM/100 kg	100	111	125	143	167	200	50 —	55.50	62.50	71 50	83 50	100.—
			abt. 0,4%/t b.d. raw material (kg)											
Na$_2$ CO$_3$ (neutralization)		20.— DM/100 kg	40	45	50	55	57	59	8.—	9.—	10.—	11.—	11.40	11.80
III Steam (15 kg/cm^2 gauge pressure)		7 — DM/t	21	22.3	24 7	26.5	27	31 2	147 —	156 —	173.—	185 —	189 —	218 —
IV Water (20° max.)		0.05 DM/m^3	120	126	132	138	144	150	6 —	6.30	6.60	6.90	7 20	7.50
V Power		0.05 DM/kWh	750	840	950	1080	1100	1150	37.50	42 —	47 50	54.—	55.—	57.50
VI Wages and Overheads		4.50 DM/h	15 h	15 h	15 h	15 h	15 h	15 h	168.—	168.—	168.—	168.—	168.—	168 —
VII Maintenance and repairs		DM/t							40.50	44.20	50.40	57.60	67.90	80 20
VIII Operating costs without amortization and interest									**557.—**	**592.—**	**1018.—**	**1126.—**	**749.—**	**1443.—**
IX Amortization and interest			yearly production (t) 300 days											
costs f. equipm. DM 3200000.—			2000						219 —					
interest rate 7%				2000						230 —				
duration 12 years					2000						240 —			
costs for buildings DM 400 000.-						2000						250 —		
interest rate: 7%		yearly amortization					2000						260 —	
duration 30 years		DM 438 000 —						2000						270.—
X Costs per ton of furfural at various yields and raw materials DM									**776.—**	**822.—**	**1258.—**	**1376.—**	**1009.—**	**1743.—**
XI By-products			quantity in t/t furfural abt						returns in DM/t furfural					
Hydrolysis waste (4500 kcal/kg)														
calculated as oil equivalent		110 — DM/t	3 2	3.7	4.3	5.1	6.1	7.7	352.—	407 —	473.—	561 —	671 —	847 —
Methanol		600 — DM/t	0.05	0.055	0.065	0.08	0.085	0.12	30 —	33 —	39 —	48 —	51 —	72 —
Acetone		600 — DM/t	0.01	0.01	0.015	0.015	0.02	0 02	6 —	6 —	9 —	9 —	12 —	12 —
XII Returns per t of furfural by by-products									**388.—**	**446.—**	**521 —**	**618.—**	**734.—**	**931.—**

Remarks

Ad I: The raw material was assumed to be agricultural waste, the costs result from transportation and wages to be paid; for wood and bagasse they correspond to the equivalent oil price

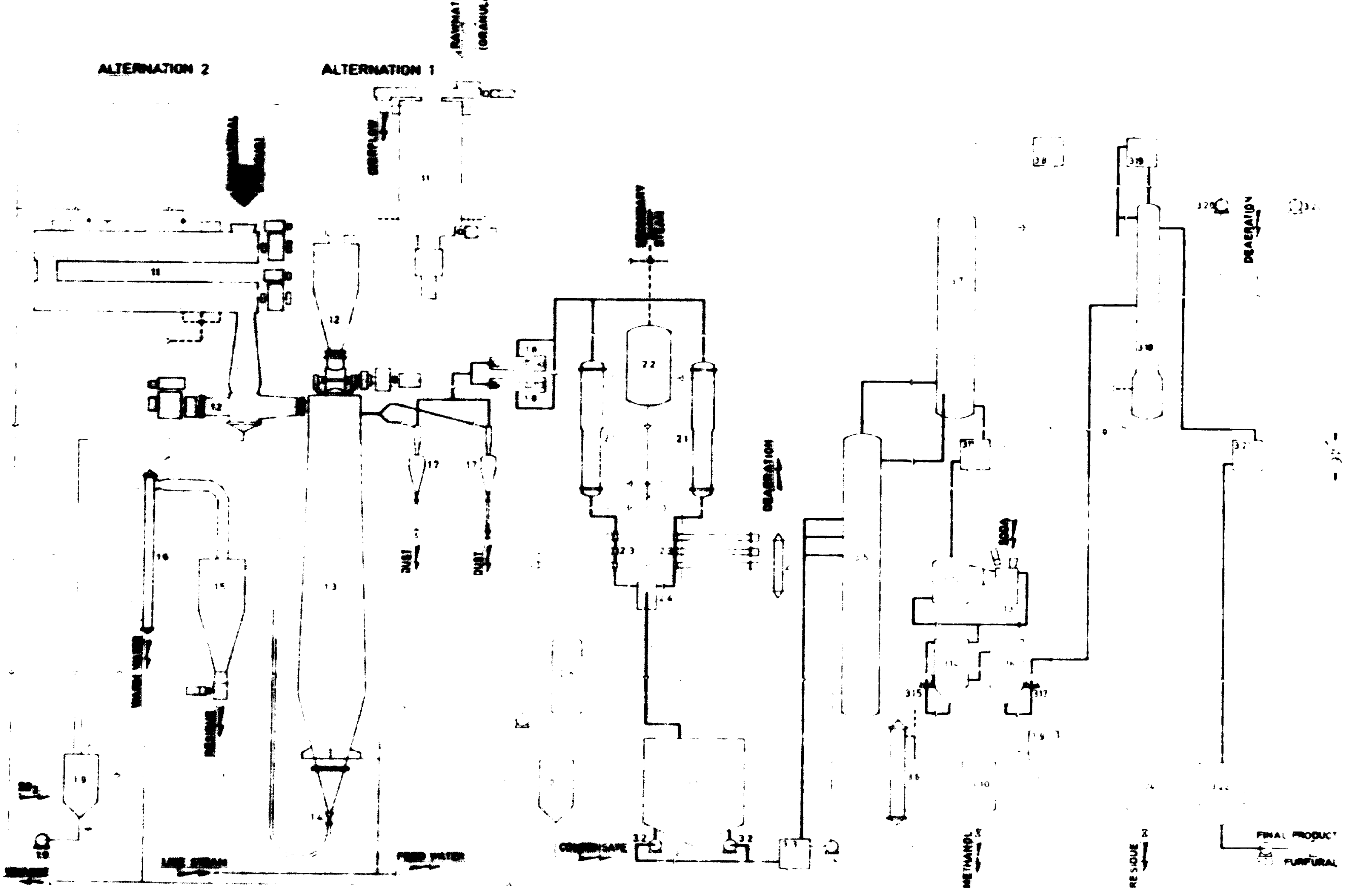
Ad III: Steam costs were calculated on the assumption that the excess steam ([illegible] atu) and the boiler feed water arising as condensate (100° C) from the column heaters will be used as make-up or boiler feed water respectively

Boiler feed water inlet [illegible]5° C
Boiler efficiency 88 %
Calorific value (Hu) kcal/kg 9700
Oil price: DM 11[illegible]-/ton
Chemicals for boiler
feed water make up DM [illegible]20/ton

Ad VI: Wages and overhead expenses only refer to the accruing costs for wages and salaries in the Furfural plant. Costs for administration work are not included

Ad IX: Value of the plant DM 3 200 000.- incl. all auxiliary plants and instrumentals. The building costs only refer to the production buildings. The costs for site purchase and site preparation and for possible sheltering of the raw material yards are not included.
The value stated for plant and buildings is to be considered an informative value for a 10% yield [illegible] with decreasing yield.

Flow Sheet of a Continuous Furfural Production Plant



b) QUAKER OATS Co Ltd. Chicago

Quaker Oats Ltd is the major producer of furfural in the world and there are nearly no publications of recent technological know-how available. (A recent communication dated January 1974 by UNIDO was answered that no licences would be sold by Quaker Oats at the moment.)

In the classical Quaker Oats process furfural is produced in a single-step operation using large rotary digesters. They are constructed of steel and lined with carbon bricks which are fitted with acid-proof cement. The raw material is charged to the rotary digesters and treated with dilute sulfuric acid. The furfural formed is removed by steam distillation. The vapors leaving the digesters are condensed and fed to a stripping column. Overhead vapors, rich in furfural, are condensed and cooled, separating into two layers. After removal of a small quantity of low-boiling heads in a methanol column, the water layer is returned to the stripping column for recovery of furfural. The furfural layer, containing about 6 % water, is sent to the dehydrating column, where the water is taken overhead, and dry furfural is drawn from the base. Distillate from the dehydrating column is sent to the stripping column decanter for recycling through the system (28, 29).

c) Oy W. ROSENLEW. Ab Pori Finland

In autumn of 1969, Oy W. Rosenlew Ab started up a 1,000-ton/yr furfural plant at its Pori mill in Finland. The new system is based on the recovery of furfural from the pentosans of birch by treating it with steam in a continuous reactor.

The input to the furfural plant is in the form of birch chips from an adjacent sulfate pulp mill, and the hydrolysis residue is blown to a continuous pulp digester. Pure furfural is obtained by distillation.

Though the plant at Pori uses birch chips, the process is very flexible and almost all pentosan containing raw materials can be used, including bagasse, almond shells, corn cobs, oat hull and processed pressed olive cakes, among others. Experience at the Pori installation has proven the effectiveness of the process.

The main equipment of the Rosenlew furfural process is the furfural reactor and the distillation columns, as shown in the flow chart on page 54 .

The raw material is fed into the preimpregnators (1). From the preimpregnators the material is fed by rotary feeders into the continuously operating high-pressure reactor (2). High pressure steam is fed into the bottom of the reactor in counter-current flow through the raw material which slowly moves downwards, and the residue is purged out at the bottom of the reactor. The level of the raw material in the reactor is regulated by a radioactive gamma-emitter which controls the hydrolysis waste purge valve. Under normal stationary conditions the residence time of the raw material in the reactor is 1 to 2 hours.

The following two consecutive reactions take place in the reactor:

$$\underset{\text{pentosan}}{(C_5H_8O_4)_n} + nH_2O \xrightarrow{K_1} \underset{\text{pentose}}{n'C_5H_{10}O_5} \quad \text{hydrolysis}$$

$$n'C_5H_{10}O_5 \xrightarrow[-\ 3nH_2O]{K_2} \underset{\text{furfural}}{n'C_5H_4O_2} \quad \text{dehydratization}$$

The hydrolysis is catalyzed by H_3O^+. This ion is formed because acetic acid and small amounts of formic acid are released from the hemi-cellulose of the raw material during special hydrolysis conditions. Thus the addition of catalyzing mineral acids which corrode the process equipment is avoided.

The steam enriched with furfural is discharged at the top of the reactor and condensed in a heat exchanger (3) generating secondary steam at about 3 at. pressure. The secondary steam delivers the process heat for the distillation columns and the excess amount is used in the boiler plant. The condensate of the furfural containing primary steam is led to the storage tank (4). The separated vapor is cooled in the condensor and returned in liquid form to the furfural storage tank. From the storage tank, furfural solution is pumped to the distillation column(5)

Furfural and water form an azeotropic mixture, the boilin point of which is 97° C and which consists of 35 weight % furfural and 65 weight % H_2O. This can be seen in Figure (page 7) showing the equilibrium curve of the H_2O-furfura system.

The formation of the azeotrop between water and furfural requires a two-stage distillation of the mixture. During the first stage the azeotropic mixture is separated and during the second the pure furfural is recovered.

The low boiling fraction (like the azeotropic mixture) is taken out of the rectifier section of the column, after which it is led to a specially designed column for further distillation. The cooled azeotrop consists of tw liquid layers, the top layer consisting of approximately 7 % and the bottom layer of approximately 95 % furfural. This can be seen in Table 2 (page 6) where the solubilit of furfural and water in each other is shown.

Furfural solution is removed from the column in form of azeotropic liquid which is cooled in the condensor and gathered to the separator (6).

In the separator the cooled azeotropic liquid is divided into two fractions. The heavier furfural solution (95 %) settles at the bottom of the tank and the lighter solution (7 %) is returned to the furfural storage (4). The furfural concentrate is neutralized with sodium carbonate.

The neutralized 95 % furfural is further purified by vacuum distillation in a packed tower column. This column is a two-part construction with the feed to the upper column where the water is removed. After this, the boiling liquid is led into the bottom column from which the pure furfural is removed and then led to the storage tank.

The low boiling fraction is distilled in a packed tower column equipped with bottom heating (9). In this column the low boiling fraction mainly consisting of acetone and methanol is separated after which the bottom distillate consisting of water and furfural is returned to the dilute furfural tank (4).

The vapor from the furfural reactor containing furfural and acetic acid is led through the regulating valve, reduced to a pressure of about 1,1 kg/cm^2, to the scrubber, where by means of furfural solution dust as well as various polymers and resins are washed in the solution. At the same time, by evaporating the solution with steam heating the furfural content of the vapor is raised near the azeotropic concentration. By filtering and withdrawing the bottom solution of the scrubber, the dust and resin content of the solution is kept at an applicable level. By means of the scrubber the vapor can be purified so that it causes no problems of getting dirtied in the packed columns or other heat exchangers of the process.

After the scrubber the vapor is led to the absorption column, where the vapor flows through the packing layers upwards, while the furfural solution impregnated with water flows downwards and absorbs the acetic acid from the vapor.

At the bottom of the absorption column the solution is evaporated in order to decrease its water content and to increase its acetic acid content. Part of the liquor which has been evaporated in this way is led to the scrubber to be evaporated, whereas the resins can be removed from the furfural circulation. The azeotrop vapor from the top of the column is led to the condensor, and the condensate from the condensor is cooled and led to the weak furfural tank, from the bottom of which the phase containing plenty of furfural is led back to the absorption column, while the phase with plenty of water is led to the furfural process to be distilled. With this phase also methanol and corresponding chemicals depart.

From the bottom of the absorption column the furfural containing acetic acid and water is led to the dehydrating column, where the solution flows down through the packing layers, while the furfural-acetic acid-vapor generated by means of the bottom vaporizer rises upwards against it. Then the water contained in the solution evaporates to the vapor phase, and waterless furfural containing acetic acid gathers on the bottom of the column. Water-furfural-acetic acid-vapor from the top of the column is led to the adsorption column.

The bottom liquid of the dehydrating column, furfural containing acetic acid is led further to the distillation column working under vacuum, to its feeding point, from which the solution flows through the packing layers downwards. The furfural vapor departing from the bottom vaporizer of the column flows through the packing layers against the solution evaporating the acetic acid from the solution. Above the feeding point the vapor still flows through the packing layers upwards, while the acetic acid returned from the condenser in the upper part flows down counter-current and adsorbs the furfural from vapor.

The furfural gathering as bottom liquid of the column is pumped with the furfural condensate from the condenser of the adsorption column to the weak furfural tank. The furfural balance of the circulation is maintained by returning a sufficient amount of furfural from the separator of the distillation column of the furfural process to the weak furfural tank.

From the upper condenser the raw acetic acid is led to the exhaust tank and pumped from there further to the

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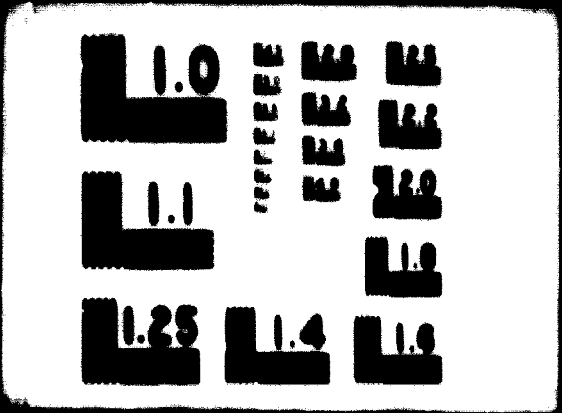


packed column, working under normal air pressure, for formic acid separation. Below the feeding point, the acetic acid from the bottom vaporizer of the column flows through the packing layers against the solution evaporating the formic acid from the solution. Above the feeding point, the vapor flows further through the packing layers at the same time as the formic acid, returned from the upper condenser, flows counter-current and adsorbs the acetic acid from the vapor.

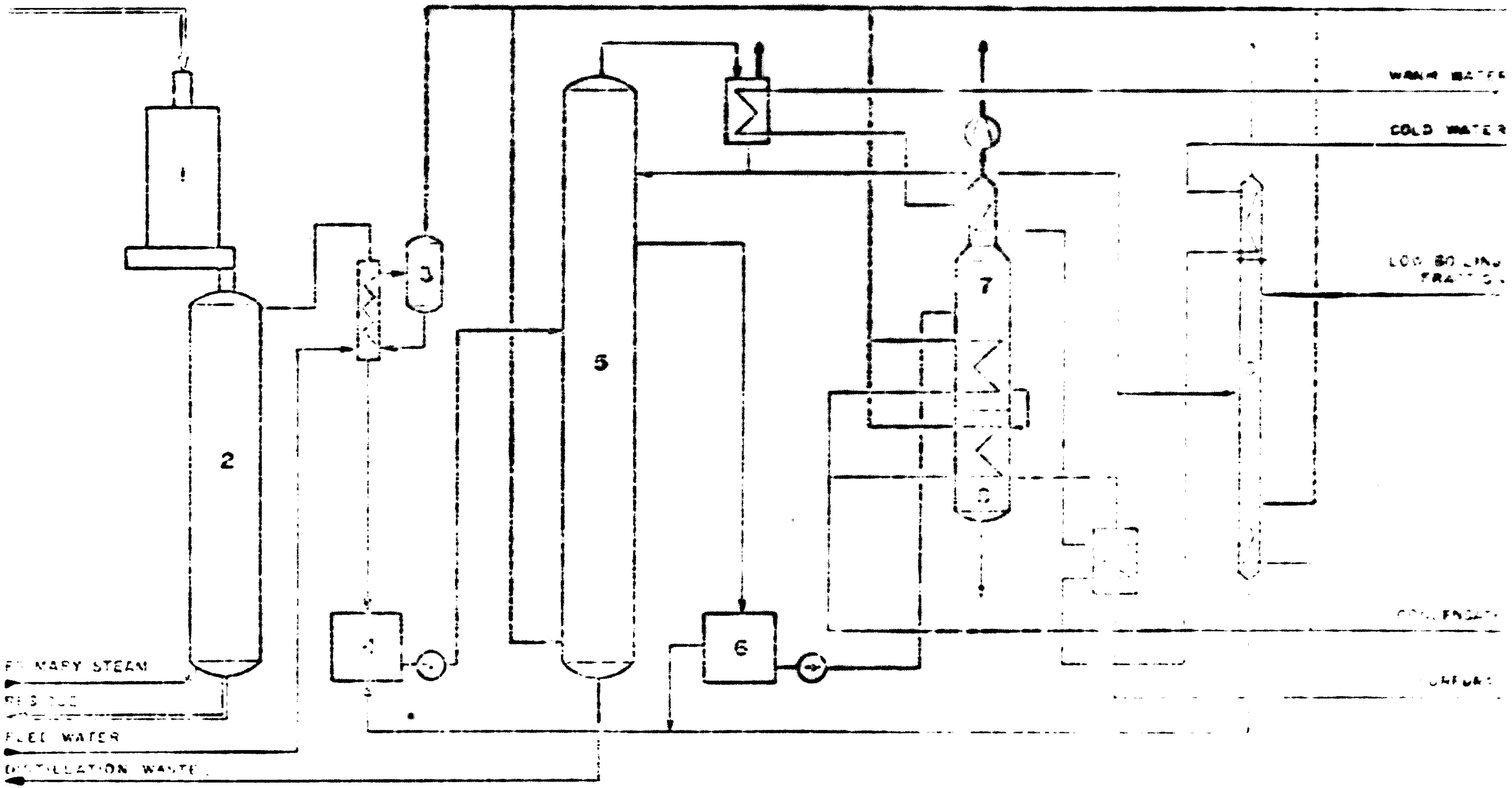
From the top of the column the condensed formic acid is led to the storage tank. The acetic acid gathering as bottom solution is pumped through the heat-exchanger to the storage tank.

This continuous furfural process is equipped with an advanced control system and has a small demand for manpower. No corrosion occurs as the process does not employ any strong mineral acid catalysts which also give polymer condensation products from furfural which may result in severe clogging of the plant equipment (30).

On page 54 you will find the process flow sheet of the Rosenlew furfural plant.

For further information, please, contact:
Oy W. Rosenlew Ab Engineering Works
28 101 Pori 10 Finland

Flow Sheet of the Rosenlew Furfural Plant



d) SIMAFER S.p.A. Milano
(new name: Compagnia Generale Impianti)

This company proposes a process using a prehydrolysis of the raw material. Hydrolysis is carried out with sulfurous anhydride as catalyst.

The corn cobs to be treated, upon arrival from the silos or storage depositories, are conveyed to a vibrating screen. The screen eliminates the sand and finer particles, while the material left on the screen is lifted, by means of a bucket elevator, to the impregnator which mixes it thoroughly with the washing solution. This solution, composed of hot water with sulfurous anhydride added, comes from the washing of the corn cobs.

From the impregnator, the mixture of corn cobs and solution passes successively into a hydrolysis tower where under proper temperature and pressure conditions the hydrolysis takes place.

After leaving the hydrolizer, a special extractor separates the solid residues from the pentosic water, the latter being sent to the conversion.

In order to recover the pentosic solution still remaining in the wastes, the latter are kneaded with hot sulphate water coming from the adscrption column.

The kneading takes place in a washer; then the washed cobs are separated from the liquid in a washing extractor. Further utilization of the exhausted cobs can be realized by burning them in a suitable steam generator; the steam thus produced can be used in the same plant, more specifically in the hydrolizers, in the conversion reactors and in the distillation column.

By means of a heat exchanger the pentosic water is cooled the heat from this being used to preheat the washing solution to be sent to the impregnator.

The pentosic water, after collection in a tank, is conveyed by a centrifugal pump to a conversion reactor, having previously passed through filters and a heat exchanger. In the reactor the pentosans are completely transformed into furfural. After leaving the reactor, the solution which contains approximately 3,5 % furfural by weight is cooled and collected in a tank.

The heat exchanger has the function of cooling the furfural containing water coming from the reactor and of preheating the pentosic water directed toward the reactor.

At this point it is necessary to eliminate the water in which the furfural is dissolved. Thus the furfural containing water is removed from the tank and sent to the distillation column, from which a technical furfural at 93 % representing the principal product of the plant, is obtained.

The technical furfural is collected in the storage tanks and sold directly. The plant however also has a discontinuous apparatus for the production of bidistillate furfural which is collected separately in a storage tank.

For further information, please, contact :

Compagnia Generale Impianti
Via Imbriani 54, Milano, Italy

Markets

Note: The figures quoted in the subsequent chapter should be considered as orders of magnitude rather than specific quantities.

Main Producers

a) U.S.A.

The Quaker Oats Ltd. is the main producer of furfural in the world. The International Petrochemicals Inc. is also one of the most important producers. Their annual production capacity is about 100,000 tons / yr but there are no published data available. The used raw materials are bagasse, corn cobs and rice husks.

The majority of their production of furfural is used in the United States or delivered to Quaker Furans NV, Netherlands, (wholly owned by the Quaker Oats Company) where furfuryl alcohol is produced. However the U.S.A. are exporting some furfural mainly to Europe and to Japan.

b) Dominican Republic

At the Romana, the Central Romana By-Products Co. Inc., a subsidiary of the South Puerto Rico Sugar Co, furfural is produced with bagasse and sugar cane.

The production capacity is estimated to be 20,000 to

25.000 tons / yr (1970). Nearly the whole production is exported to the U.S.A.

c) Argentina

The Indunor S.A. produces furfural as a by-product in the production of tanning extracts. The annual production capacity is about 1,800 tons / yr (1970). The majority of this furfural production is used in the oil refining industry.

d) France

There are two furfural producing companies : Agrifurane has a production capacity of about 4,000 to 5,000 tons per year and Sicamie produces 3,000 tons / yr (1970). The first mentioned company uses corn cobs as raw material, the second produces furfural as a by-product in the cellulose manufacture.

Furfural is mainly used in oil refining and by the "Usines de Melle" the latter to produce furfuryl alcohol. However the national production is insufficient to the interior needs, thus France has to import about 2,000 tons / yr (1970) of furfural. The exports vary between 400 and 1,000 tons per year (1970).

e) Italy

Here furfural is produced by two companies: Ledoga S.p.A. and Società Italiana di Furfurolo.

It seems that the total production of these two companies is around 8,000 tons / yr (1970) but no exact data are available. Raw materials are extracts of edible chestnuts, rice husks and residues of olives.

The local production quantity is nearly sufficient to cover the internal needs and therefore there are no imports. On the other hand the exports vary from 850 to 1,600 tons / yr (1970).

f) Spain

The Furfural Espanol SA produces about 1,000 tons / yr from olive kernels. There are also other producers of less importance. The PROFURSA (Produccion de Furfural y Derivados SA) constructed a new furfural plant with a capacity of 5,000 tons / yr which uses almond shells as raw material.

g) Finland

The Oy W. Rosenlew produces some 1,000 tons of furfural per year (1970), starting with birch wood.

h) Hungary, Czechoslovakia and Yugoslavia

These three countries produce furfural with pulp or sun flower as raw material. There are no production data available but it seems that production varies mainly because of technical difficulties.

i) Soviet Union

The Soviet Union is a large furfural producer. Minimum production is estimated to be 6,000 tons / yr (1970).

j) People's Republic of China

In this country production is assumed to be about 7,000 tons per year (1970). No information is available on the raw material used and internal uses. China is exporting furfural mainly to Japan, to Western Germany and to France.

k) Japan

The Sumitomo Chemical Co. produces furfural. Capacity is assumed to be 1,500 tons / yr (1970).

l) India

The M/s Natson Manufacturing Co. Pvt. Ltd. in Ahmedabad produces 700 tons /yr. Full plant capacity is 1,800 tons per year.

International Market Situation

Main exporting countries are the Dominican Republic, China, U.S.A., Italy, France and Soviet Union. Main importing countries are the U.S.A., the German Federal Republic, Japan, France, Belgium, Netherlands and the U.K.

The world trade data are as variable as those for the production. You will find at the end of this chapter additional statistic material concerning the main import and export countries.

Over the past 10 years or so the world market for furfural has been uncertain and erratic. In the early 1960's, for example, the world market was adequately supplied by existing producers - mainly the U.S.A. However, the wet autumn of 1964 in the U.S.A. damaged a considerable quantity of the maizecob husks - one of the principal raw materials - and the ensuing furfural shortage was aggravated the following year by a revolution in the Dominican Republic which interrupted production in that country. Partly on account of these incidents Du Pont of the U.S.A. planned plant to produce tetrahydrofuran by-passing furfural. Since the mid 1960's, furfural plants have come on stream in Florida (Quaker Oats Ltd.), in Texas (International Petro-Chemicals Ltd.) and in Finland (OY W. Rosenlew). These developments have more than covered the reduction in capacity caused by the closure of small units in Europe.

Investigation into the furfural market indicates that there is little consensus of opinion on the present and future situations. Impressions gained vary from company to company depending upon their interest and involvement in the furan chemical industry. One large chemical manufacturer who is not concerned with profits from furfural production so much as having a reliable source for making furfural derivatives commissioned a market research report on furfural and its derivatives. The conclusion , corroborated by the company's own findings, was that the market was growing very slowly and that, in the light of existing and planned new capacity, there would be excess capacity which would result in a fall in price. As a result the firm seems to be making no effort to enter furan chemical production.

World production of furfural and the manufacture of furfuryl alcohol is dominated by Quaker Oats Ltd. who are of the opinion that the market is growing, especially for furfuryl alcohol and its derivatives, and are planning more capacity for the alcohol. Their optimistic view of the market in the future is expressed by the fact that, although their U.K. alcohol plant is working below full capacity, they are putting on stream further capacity and admit that they are in a calculated over-capacity situation which is likely to be the position for several years to come. The world price for furfural, especially in the U.S.A. and Western Europe, is highly dependent upon this major producer which can force up the price by withholding output, and by choosing to operate at full capacity it can induce a fall in prices. Thus a new producer is unlikely to be able to enter the furfural market unless he can obtain a long term contract to sell and this would have to be at a price below that normally quoted.

One firm has started to make inroads into the U.K. market by selling the Finnish production below the normally quoted price. The Finnish furfural is claimed to be of superior quality being pale in colour and over 99 % pure. This company is of the opinion that the world market could absorb another 5,000 tons per annum of furfural at a price under that normally quoted.

On account of some important furfural consumers switching to synthetic processes (for example Du Pont Co.) and because of planned and proposed new plant in Puerto Rico and Finland respectively, potential supply in the future seems to exceed demand by about 20,000 tons a year, which with a total world market of about 150,000 tons a year is a significant proportion. In a free market situation one would expect a fall in price and in mid 1968 Quaker Oats Ltd. forecast a fall in the European price of about one third when the Finnish output reached the market. Given the limited number of firms at present engaged in furan chemicals production on a large scale, there is always the possibility that prices can be maintained at a higher level than would be realized in a freer market; on the other hand, if existing plants were operated at full capacity, there would be probably a downward pressure on prices.

The opinion of one company was that a new producer would do better by manufacturing the alcohol since it foresaw a stronger demand for this rather than furfural itself. Three important factors may mitigate against this however:

a) the alcohol production requires considerable additional capital outlay - almost as much again as a furfural plant;

b) the alcohol production process requires fairly cheap supplies of hydrogen;

c) in the developed countries - i.e. in the major markets - furfuryl alcohol tariffs are, on the whole, higher than those on furfural, although new producers in the Commonwealth would benefit from Commonwealth Preference in the U.K. market.

The Quaker Oats company is interested in all potential new sources of supply; it would therefore be very interested to hear more about any new proposals for furfural production and the firm would be prepared to investigate further the feasibility of a scheme required.

It appears that the aforementioned firms regard the market for furfural and its derivatives as favorable only on account of their present involvement. The prospects for a new and independent producer are not really good unless long term contracts for the output could be guaranteed, several small plants in Europe having had to cease operations within the last five to ten years.

a) Consumption

As no exact figures for the world furfural production are available it is not possible to evaluate exactly the world furfural consumption. Nevertheless, the total furfural consumption can be estimated to exceed 150,000 tons per year. As indicated above it is impossible to give a detailed survey of the utilization of furfural, but the four main uses

- as starting material for the production of furfuryl alcohol, tetrahydrofurfuryl alcohol, tetrahydrofuran and other derivatives;
- as reactive solvent in the production of furfural-phenol resins;
- as selective solvent for the separation of paraffins and aromatic compounds in lubricating oil refining;
- as solvent in the extraction of butadiene

seem to be the most important both at present and in the future. The most rapidly developing market is the one which uses furfural in the production of furfuryl alcohol the latter being used - as mentioned above - in the manufacture of resins.

b) Price History

From 1960 to 1965, the prices have been stable till the great shortage of furfural in 1965. The reasons for this shortage are not completely enlighted. Officially, as mentioned above, it was due to the bad meteorological conditions which damaged a considerable quantity of the maizecob husks and due to the events in the Dominican Republic in 1966. During this period of furfural shortage Quaker Oats Ltd. developed its production but the prices rose up by 20 %. At the end of 1969 the prices again moved upwards in the U.S.A.

According to the European Chemical News dated from 14/8/1970 the prices have been:

Furfural, in lots of 5 tons, including transport costs:

U.S.A.	Belgium		France	
cents/lb	FB/kg	cents/lb	FF/kg	cents/lb
16	20,90	19,1	1,85	15,4

Fed. Rep. Germany		Italy		United Kingdom	
DM/kg	cents/lb	Lit/kg	cents/lb	pence/lb	cents/lb
1,54	19,1	302	23,1		21,50

These prices are to be understood without local taxes, except for Italy.

Recent furfural prices (November 1973) are:

U.S.A.	18,75	¢ / lb
Belgium	24,50	FB / kg

Federal Republic of Germany	1,54	DM / kg
Italy	290	Lit / kg
United Kingdom	22.40	£/100 / kg

The price for furfuryl alcohol was 18,25 ¢ / lb (1970, east of Denver)[+].

However, as furfural prices vary considerably it is not possible to make any presumptions for the future.

The tetrahydrofuran prices in lots of one ton including transport costs were (according to European Chemical News dated from August 1970):

U.S.A.	Belgium		France	
cents/lb	FB/kg	cents/lb	FF/kg	cents/lb
37,50	38,80	35,40	5,50	45,80

Fed. Rep. Germany		Italy		United Kingdom	
DM/kg	cents/lb	Lit/kg	cents/lb	pence/lb	cents/lb
2,79	34,7	620	45,3	45	

[+]) Oil, Paint and Drug Reporter, 4/8/1970.

c) Marketing

1) Quality. Furfural quality is a very important factor. For most applications it has to be extremely pure. Its degree of purity normally is higher than 98 %. New producers would have to respect this demand of high quality and buyers will order samples for quality control.

2) Rates of Duty. Import and export taxation is shown in the tables 6, 7, 8, 9 and 10 (recent changes not considered).

Table 6

Rates of Duty

Country	Furfural	Furfuryl Alcohol	Remarks
U.K.	12,5 % (1972)	25 %	preferential rate
U.S.A.	0	2,4 ¢/lb of weight + 12 % ad valorem	
EEC	7 % ad valorem (1972)	13,6 %	plus other taxations ranging from 7 % to 23,65 % depending upon country
Japan	10 % ad valorem	not given	
Australia	7,5 %	7,5 %	preferential rate - free to U.K., N.Z., Canada and some other Commonwealth countries
Sweden	9 % ad valorem (1972)	not given	
Norway	15 % ad valorem (1972)	not given	

Table 6 continued

Country	Furfural	Furfuryl +) Alcohol	Remarks
South Africa	10 % ad valorem		
Brazil	15 %		
Argentina	90 % ad valorem		

+) November 1969

Table 7

Dominican Republic - Exports of Furfural

	1966		1967	
	Quantity (Tons)	Value (US $)	Quantity (Tons)	Value (US $)
Total	14,740	3,725,482	14,430	4,126,503
U.S.A.	12.600	2,989,373	13.200	3,717,046
Venezuela	429	142,128	487	156.548
Trinidad & Tobago	113	37.500	366	125.262
Netherlands Antilles	479	158,434	337	106,868
France	458	156,515	-	-
U.K.	267	99,663	55	15,720
Japan	239	80,493	-	-
Netherlands	163	61,376	-	-

Table 8

Federal Republic of Germany - Imports of Furfural

	(1968)	Tons
Total		3,043
of which -	U.S.A.	1,280
	China	920
	U.S.S.R.	600
	E.E.C.	240

Average Value of imports : US $ 290.--

Table 9

Federal Republic of Germany - Imports of Furfuryl Alcohol Tetrahydrofuran and Derivatives

	(1968)	Tons
Total		4,613
of which -	Belgium - Luxembourg	3,400
	U.S.A.	550
	Other E.E.C.	530

Average value of imports : US $ 480.--

Table 10

Italy - Exports of Furfural and Imports of Furfuryl Alcohol, Tetrahydrofuran and Derivatives (1967)

Exports of furfural : 850 tons at an average value of 580 US $ per ton.

Imports of furfuryl alcohol, tetrydrofuran and derivatives :

Total		1,640 tons
of which -	U.S.A.	1,200 tons
	France	340 tons

Average value of imports : US $ 630.--

3) Distribution. In Western Europe and in the U.S.A. distribution circuits generally are very short. Final users normally buy directly from the producer (or his representative) or from the importer. In those countries, whose own production is not sufficient, the end users do not import themselves but buy from importing firms with better storage facilities.

4) Stock-keeping and Transporting. Furfural quality changes rapidly and therefore stock-keeping is not easy. Exposed to the air and to light, furfural becomes yellow to brown coloured. Even stored in hermetic steel tanks the product changes its colour after some time. This has to be taken into consideration if transport out of the country is

envisaged. Furfural is transported in tank-trucks or tank-wagons or in barrels (capacity from 20 to 200 liters). The containers have to be constructed of acid proof stainless steel. Beside this they have to be absolutely hermetic (27).

5) Statistics. On the following pages you will find a survey concerning the imports and exports of furfural by several countries over the period from 1965 to 1969.

Table 11

IMPORTS OF FURFURAL BY BELGIUM

value c.i.f.

from country	1965[a]		1966		1967		1968		19[illegible]	
	quantity kg	value $	quantity kg	value $	quantity kg	value $	quantity kg	value $	quantity kg	value $
France	-	-	10 200	21 000	-	-	5 600	[illegible]	22 [illegible]	[illegible]
F.R.Germany	5 000	7 500	20 200	24 000	-	-	-	-	[illegible]	[illegible]
Italy	-	-	25 [illegible]00	31 000	21 500	10 000	-	-	-	-
Netherlands	20 300	35 000	-	-	23 300	6 000	-	-	-	-
U.K.	-	-	-	-	-	-	14 800	[illegible]	-	-
U.S.A.	-	-	-	-	-	-	220 900	54 [illegible]	21 100	[illegible]
P.R.China	-	-	9 400	6 000	-	-	-	-	[illegible]	[illegible]
Dominican Rep.	-	-	-	-	-	-	-	-	[illegible]	[illegible]
others	6 600	9 500	9 800	13 000	41 200	15 000	49 200	25 50[illegible]	[illegible]	[illegible]
Total	31 900	52 000	73 [illegible]	95 000	86 000	31 000	290 500	[illegible] 000	[illegible]	[illegible]

[a]) **Furfural and benzofurane; however, imports of benzofurane are of less importance** in the following **years**

Source: Bulletin mensuel du commerce extérieur de l'Union économique belgo-luxembourgeoise.

Table 12

IMPORTS OF FURFURAL BY FRANCE

value c.i.f.

from country	1965		1966		1967		1968		1969	
	quantity kg	value $	quantity kg	value $	quantity kg	value $	quantity kg	value $	quantity kg	value $
Italy	823 000	240 000	373 000	192 000	68 000	29 500	88 000	28 000	130 000	[illegible]
CSSR	110 000	35 000	74 000	22 500	31 000	15 000	[illegible]	16 500	-	-
U.S.A	200 000	58 000	-	-	-	-	32 000	11 500	171 000	[illegible]
P.R.China	1 624 000	330 000	1 183 000	481 000	4 056 000	1 008 000	1 098 000	290 500	1 584 000	[illegible]
Hungary	-	-	65 000	56 000	27 000	10 500	-	-	-	-
USSR	942 000	288 000	157 000	50 000	-	-	-	-	-	-
Dominican Rep.	560 000	130 000	456 000	195 000	-	-	-	-	-	-
Switzerland	41 000	13 000	-	-	-	-	-	-	-	-
Spain	-	-	-	-	-	-	-	-	148 000	35 500
others	20 000	11 000	22 000	10 500	2 000	3 000	29 000	10 000	32 000	8 500
Total	4 318 000	1 105 000	2 273 000	1 007 000	4 184 000	1 066 000	1 343 000	356 500	2 065 000	443 500

Source: Statistiques du Commerce extérieur de la France.

Table 13

IMPORTS OF FURFURAL BY THE GERMAN FEDERAL REPUBLIC
value c.i.f.

from country	1965*		1966*		1967		1968		1969	
	quantity kg	value $	quantity kg	value $	quantity kg	value $	quantity kg	value $	quantity kg	value $
France	1 954 700	971 500	775 40	577 000	50 000	11 500	35 600	15 000	[illegible]	[illegible]
Belgium / Luxembourg	-	-	-	-	50 500	21 500	22 900	11 000	12 [illegible]	[illegible]
Netherlands	2 200	5 000	-	-	132 000	55 000	-	-	[illegible]	[illegible]
Italy	116 700	53 000	182 40	136 500	165 200	35 600	185 000	47 500	[illegible]	[illegible]
CSSR	128 600	26 000	239 10	147 000	56 900	23 000	39 700	8 100	-	-
Hungary	15 300	4 000	-		20 600	5 000	-	.		
U.S.A.	1 841 300	754 000	2 399 [illegible]	1 [illegible] 000	1 957 [illegible]	395 500	1 265 100	330 000	1 37[illegible]	[illegible]
P.R. China	29 500	6 000	[illegible]	76 000	1 011 500	454 500	921 100	250 500	[illegible] 700	[illegible]
USSR	1 682 800	352 000	1 440 80	86 000	-	-	600 600	144 000	450 000	[illegible]
Spain	-	-	-	-	-	-	-	-	25 500	[illegible]
Japan	357 000	177 000	366 10	132 000	-	-	-	-	-	
U.K.			22 [illegible]	7 000						
Yugoslavia			90 700	69 000						
Total	5,828,100	2,378,500	6 562 100	3 987 300	3 380 900	1 290 000	3 090 400	941 500	3 449 800	905 000

*) including cumarone, furfural and tetrahydrofurfuryl alcohol, thiophene - imports of which having been considerably higher than those of furfural itself.

Table 14

IMPORTS OF FURFURAL, IN NETHERLANDS - Value c.i.f.

from country	1965[a]		1966		1967		1968		1969	
	quantity kg	value $	quantity kg	value $	quantity kg	value $	quantity kg	value $	quantity kg	value $
France	104 000	56 000	332 000	173 000	522 000	226 000	295 000	88 000	293 000	27 000
F.R.Germany	45 000	15 000	243 000	195 000	-	-	34 000	10 000	-	-
Italy	205 000	13 000	544 000	300 000	377 000	190 000	604 000	244 000	389 000	144 000
Belgium	-	-	2 000	2 000	131 000	47 000	507 000	151 000	178 000	58 000
USSR	290 000	73 000	11 000	10 000	319 000	95 000	10 000	3 000	212 000	45 000
U.S.A.	320 000	152 600	359 000	120 000	47 000	16 000	-	-	-	-
Dominican Rep.	10 000	23 000	135 000	57 000	-	-	-	-	-	-
P.R. China	30 000	7 000	126 000	100 000	10 000	4 000	86 000	21 000	15 000	3 000
CSSR	-	-	-	-	140 000	41 000	-	-	-	-
Spain	-	-	6 000	5 000	-	-	-	-	19 000	6 000
Switzerland	-	-	37 000	9 000	-	-	-	-	7 000	2 000
Total	1 309 000	404 600	1 795 000	971 000	1 546 000	619 000	1 536 000	517 000	1 311 000	[illegible]

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[a] Furfural and benzofurane; however, imports during the following years have been negligible.

Table 15

IMPORTS OF FURFURAL BY BRASILIA - value c.i.f.

from country	1965		1966		1967		1968		1969	
	quantity kg	value $	quantity kg	value $	quantity kg	value $	quantity kg	value $	quantity kg	value $
U.S.A.	137 300	46 832	115 229	49 785	94 041	41 023	66 371	38 727	-	-
France	2 840	1 472	11 960	11 721	-	-	10 000	5 250	-	-
Italy	-	-	-	-	18	106	19	169	-	-
F.R.Germany	-	2	2	50	4	93	-	3	-	-
Netherlands	-	-	15	67	5	27	15	33	-	-
Switzerland	1	4	-	-	2	23	-	-	-	-
Israel	-	-	200	1 277	-	-	-	-	-	-
U. K.	-	-	-	-	-	-	5	12	-	-
Total	140 141	48 310	127 406	62 900	94 070	41 272	76 410	44 144	-	-

Source: Comercio Exterior do Brasil Vol.I - Importacao por mercadorias, segundo os paises Servicio de Estatistica economica e financeira, Ministerio da Fazendra.

Table 16

IMPORTS OF FURFURAL BY JAPAN - value c.i.f.

From country	1965		1966		1967		1968		1969	
	quantity kg	value $	quantity kg	value $	quantity kg	value $	quantity kg	value $	quantity kg	value $
P.R. China	1 436 324	397 274	1 253 960	646 154	1 682 590	448 265	1 888 100	470 964	2 201 942	502 370
U. S. A.	-	-	-	-	542 539	189 422	107 782	40 643	170 625	63 214
Dominican Rep.	-	-	-		238 653	92 152	-	-	-	-
Total	1 436 324	397 274	1 253 960	646 154	2 463 782	729 839	1 995 882	511 607	2 372 567	565 584

Source: Japan Exports and Imports, Japan Tariff Association.

Table 17

EXPORTS OF FURFURAL FROM FRANCE - value f.o.b.

to country	1965 quantity kg	1965 value $	1966 quantity kg	1966 value $	1967 quantity kg	1967 value $	1968 quantity kg	1968 value $	1969 quantity kg	1969 value $
Netherlands	69 000	34 000	393 000	192 000	463 000	207 000	315 000	96 000	293 000	75 000
Belgium/Luxembg.	-	-	-	-	833 000	306 500	-	-	130 000	34 500
Italy	-	-	-	-	-	-	-	-	102 000	29 000
F.R.Germany	53 000	17 000	32 000	24 000	30 000	11 000	-	-	90 000	29 500
U. K.	11 000	12 000	20 000	13 000	-	-	-	-	-	-
U.S.A.	-	-	90 000	80 000	-	-	-	-	-	-
Argentina	-	-	-	-	-	-	-	-	50 000	16 000
Venezuela	50 000	23 000	-	-	-	-	-	-	-	-
Netherlands Ant.	60 000	69 000	-	-	-	-	-	-	-	-
Mexico	-	-	-	-		12 000	-	-	-	-
Australia	-	-	53 000	47 000	-	-	-	-	-	-
Israel	-	-	109 000	62 000	-	-	-	-	-	-
others	-	-	-	-	51 000	31 000	75 000	44 000	-	-
Total	15 000	12 000	19 000	12 000	95 000	22 000	18 000	10 000	16 000	8 000
	258 000	167 000	716 000	430 000	1 417 000	591 500	408 000	150 000	701 000	192 000

Source : Statistiques du commerce extérieur de la France.
Direction générale des Douanes et droits indirects du Ministère de l'économie et des finances.

Table 18

IMPORTS OF [illegible] FROM IT[illegible] value [illegible]

country	1965		1966		1967		1968		1969	
	quantity kg	value $	quantity kg	value $	quantity kg	value $	quantity kg	value $	quantity kg	value $
Netherlands	-	-	318 060	175 000	457 025	212 000	640 266	246 000	-	-
W.K. Germany	-	-	135 200	95 000	108 212	41 000	185 000	49 000	-	-
France	8 749	258	401 575	215 000	45 035	20 000	37 805	26 000	-	-
Belgium	-	-	6 027	5 000	24 000	11 000	10 940	[illegible] 000	-	-
Spain	-	-	35 [illegible]	32 000	60 172	57 000	322 930	87 000	-	-
Greece	-	-	9 050	7 500	40 052	15 000	59 110	21 000	-	-
Switzerland	-	-	11 660	8 500	35 000	6 000	45 000	16 000	-	-
Austria	-	-	[illegible]	20 000	20 700	13 000	19 080	8 000	-	-
Yugoslavia	-	-		-	15 050	7 000	50 000	10 000	-	-
Israel	-	-	75 080	49 000	20 040	8 000	10 740	5 000	-	-
Iran	340	33		-	-	-	278 365	72 000	-	-
Iraq	-	-	81 120	89 000	-	-	-	-	-	-
India	-	-	250	500	-	-	521	1 500	-	-
Pakistan	-	-	63 002	58 000	33 840	16 000	-	-	-	-
Zaïre	-	-	11 110	9 000	-	-	-	-	-	-
South Africa	-	-	9 000	7 000	11 500	9 000	-	-	-	-
U. K.	-	-	139 155	125 500	10 180	13 000	-	-	-	-
U.S.A.	-	-	92 420	85 000	-	-	-	-	-	-
Argentina	-	-	80 320	69 000	4 575	6 000	-	-	-	-
[illegible]										
others	6 212	284	139,501	134,000	5 923	16 000	6,835	36,500	-	-
Total	15 301	575	1 632 981	1 179 000	850 294	430 000	1 637 533	582 000	-	-

Source: Statistica annuale del Commercio con l'estero, Istituto centrale di Statistica, Rome.

Table 19

EXPORTS OF FURFURAL FROM THE DOMINICAN REPUBLIC - value f.o.b.

to country	1963		1964		1965		1966		1967	
	quantity kg	value $	quantity kg	value $	quantity kg	value $	quantity kg	value $	quantity kg	value $
U.S.A.	15 300 896	3 252 623	12 368 789	2 550 466	9 186 049	1 930 959	12 817 620	2 989 37[illegible]	13 812 518	3 727 095
Trinidad/Tobago	348 122	37 693	697 511	128 227	408 619	103 096	113 390	[illegible] 500	366 507	[illegible]
Netherlands Ant.	415 602	97 398	749 623	150 748	744 123	137 935	879 097	135 43[illegible]	537 097	106 [illegible]
Venezuela	443 079	90 272	930 96[illegible]	187 224	198 564	59 976	429 76[illegible]	142 12[illegible]	457 218	156 [illegible]
F.R.Germany	68 467	9 620	110 69	10 050	-	-	-	-	-	
France	1 425 366	205 475	219 138	32 652	498 010	98 623	448 026	156 535	-	-
Netherlands	50 130	7 604	15 226	3 739	268 709	55 120	165 594	61 516	-	-
U. K.	751 455	107 288	746 51[illegible]	115 515	275 913	45 250	267 356	99 663	55 887	[illegible]
Japan	542 924	80 265	448 52	74 103	-	-	259 415	80 495	-	-
Australia	1 173 679	206 722	-	-	66 649	13 416	-	-	-	-
Total	20 789 158	4 209 78[illegible]	17,233,6[illegible]	3 257 614	11 647 635	2 429 525	14 366 594	3,725,452	14 639 299	[illegible]

List of Furfural Producers

U.S.A.

The Quaker Oats Company, Chemicals Dept.
Merchandise Mart Plaza
Chicago 54, Illinois

International Petro-Chem., Inc.
Lafayette, Louisiana

Dominican Republic

Central Romana By-Products Co., Inc.
la Romana

Argentina

Indunor S.A.
Leandro N. Alem - 896
Buenos Aires

France

Société Agrifurane
34, Av. de Messine, 75, Paris 8^e

Société Sicamie
27 - Alizay

Italy

Società Italiana di Furfurolo S.p.A.
8, Via Albricci, 036 Milano

Ledoga S.p.A.
Via Roberto Lepetit, 036 Milano

Spain

Furfural Espanol, S.A.
Alcantarilla (Murcia) y Amposta (Tarragona)

Profursa S.A.
37, Via Layetano, Barcelona

Finland

Oy W. Rosenlew Ab, Engineering Works
Pori

German Federal Republic

Schwäbische Zellstoff AG
Ehingen / Donau

Japan

Sumitomo Chemical Co Ltd.
15, Kitahama 5 - Chome-
Higashi - Ku - Osaka

India

M/s Natson Manufacturing Co Pvt. Ltd.
Ahmedabad

List of Furfural and Furfural Derivatives Consumers

U.S.A.

Acme Resins Corp.
Forest Park Ill. (furan resins)

Aristo Division, Imc Corp.
590 E. Davison at Clough
Detroit Michigan (largest supplier of "hot-box"
foundry resins)

Ashland Chemical Co.,
Division of Ashland Oil & Refining Co.,
Eight East Long Street,
Columbus Ohio 43216
(largest supplier of "no-bake"
foundry resins)

Borden Chem. Co.,
350 Madison Avenue
New York N.Y. 10017
(furan resins, phenolic resins)

Carborundum Co.,
Bonded Abrasives Div.,
Niagara Falls, N.Y.
(coated abrasives, grinding wheels
graphite rods)

Durez Division
Hooker Chemical Corp.,
North Tonawanda, N.Y.
(foundry resins,chem.resistant
bricks)

Furane Plastics Inc.,
5121 San Fernando Road West
Los Angeles, Calif. 90039
(furan resins)

G. E. Smith,
4 - A West Manilla Avenue
Pittsburg, Pa. 15220
(foundry resins)

Haveg Industries Inc.,
Chemical Equipment Division
900 Greenbank Road,
Wilmington, Del. 19808
(chemically resistant mortars)

U.S.A. cont'd.

Houghton, E.F. & Co.,
305 West Lehigh Ave.,
Philadelphia Pa. 19133
(furan resins)

3M Co.,
2501 Hudson Road
St Paul 19, Minn.
(coated abrasives)

Reichhold Chemicals
523 North Broadway,
White Plains, N.Y. (foundry resins; phenolic moulding resins)

Norton Co.,
50 New Bond Street
Worcester Mass. 01606
(abrasives, grinding wheels)

Synvar Corp.,
917 Washington Street,
Wilmington Del. 19899
(foundry resins; plywood adhesives)

United Kingdom

Ashland Chemical Ltd.,
Forge Lane, Halesowen
Birmingham

Aske & Co., Ltd.,
Victoria Works, Waterside
Halifax, Yorks.

Borden Chemical Co., (U.K.) Ltd.,
North Baddesley
Southampton

Catalin Ltd.,
54 Farm Hill Road, Waltham Abbey,
Essex

F & M Suppliers Ltd.,
8 - 9 Hayne Street, Charterhouse Square,
London, E.C. 1.

United Kingdom cont'd.

Fordath Ltd.,
Brandon Way,
West Bromwich, Staffs
(one of the largest suppliers of foundry resins in U.K.)

Mitchell, W.A. & Smith Ltd.,
Church Path, Church Road,
Mitcham, Surrey (chemically resistant mortars)

Berk Ltd.,
Berk House, 8 Baker Street
London W.1 (jobbers)

Tar Residuals Ltd.,
Plantation House,
Mincing Lane
London E.C. 3. (jobbers)

Netherlands

Nederlandse Castorolie Fabriek Necof,
P.O. Box 6,
Geertruidenberg (important manufacturer of foundry resins)

France

Soc. Sapic,
Le Clos Barrois, Quai d'Amont-Creil (60)
(important manufacturer of foundry resins)

Federal Republic of Germany

BASF
Ludwigshafen / Rh., (very large furfural user)

Farbwerke Hoechst
Frankfurt / Main - Hoechst
(chemically resistant mortars)

Dr. F. Raschig GmbH
Ludwigshafen / Rh., (largest supplier of foundry resins)

Federal Republic of Germany (contd.)

Hüttenes - Albertus, Chem. Werke GmbH
Düsseldorf - Heerdt, Wiesenstr. 23/64
(important supplier of foundry resins)

Imperial - Oel - Import Küers & Co.,
Hamburg 1,
Bergstrasse 11 (jobbers)

Keramchemie
Siershahn, Westerwald
(chemically resistant mortars, bricks)

Outlook

Today the great furfural shortage during 1965/66 is surmounted. Production capacity steadily has raised and it is probable that the furfural market will develop slowly but steadily during the next years. No sudden increase of demand is expected but the production of furfuryl alcohol, which is used in the manufacture of foundry resins, has shown an extraordinary growth rate due to new technologies in making cores and moulds.

But also the utilization as solvent equally will be important.

On the other hand it is possible that in some cases furfural will be replaced by other chemical products in new processes, as tetrahydrofuran production from Du Pont has shown.

To surmount those difficulties, it is recommendable to new furfural producers to combine furfural production either with the production of furfuryl alcohol or with the production of paper or cellulose, as in these cases furfural appears as a low-priced by-product.

Investment costs for a plant using bagasse as raw material and a capacity of 5,000 tons per year may be between

1 and 3 million dollars (no exact data can be given due to the rapid price changes during the last years). This calculation does not include the yearly expenses which depend on salaries, steam-, water-, container- and transport-costs. If furfural production is not independent but part of e.g. paper production, production costs will be low and profits high. Steam-costs and feed-water-costs are of great importance as for the production of 1 kg furfural about 25 kg of steam are necessary (depending on process used).

The more usable by-products there are, the more interesting furfural production becomes.

According to the storage difficulties, which have been mentioned above, furfural should be sold as fast as possible. Thus it is recommended to envisage a cooperation with Quaker Oats (the main furfural producer) or with another company, if the local market can not absorb a considerable amount of the production. Furthermore, to prevent a decrease in quality during long distance transports it seems to be useful to export mainly to the neighbouring countries.

Nevertheless furfural production may be of considerable interest in the future as it offers the possibility to manufacture organic solvents and a starting material in polymer synthesis by-passing petroleum.

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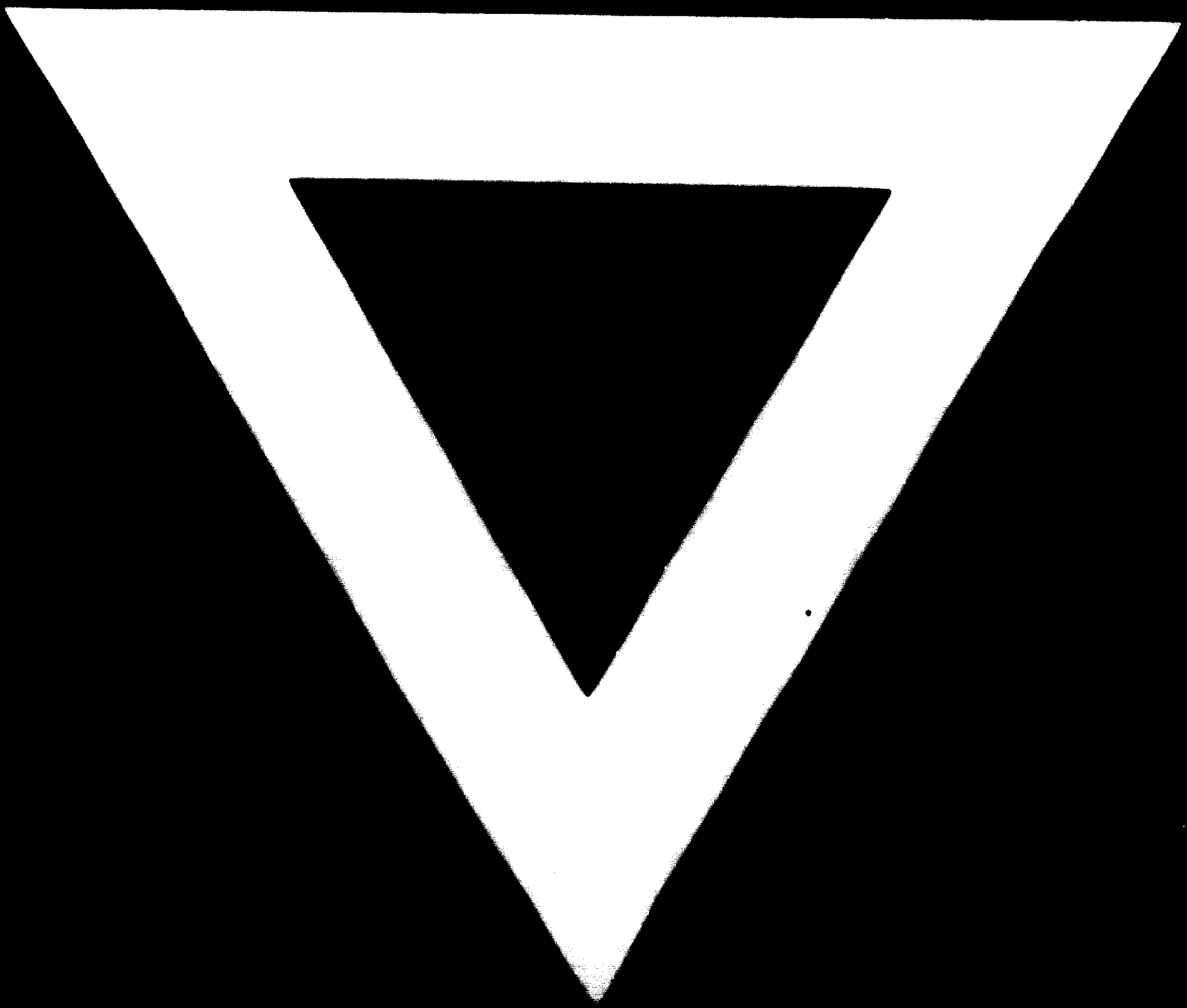

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