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Furfural – Gold from Garbage

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Abstract

Furfural production using continuous feeding process was discussed by using the Westpro modified Chinese Huaxia Furfural Technology as an example. The technical process, equipment required, raw materials needed, unit operations, operation parameters, operation staff, available byproducts, economic considerations, possible markets, and land area considerations are mentioned. The production and uses of some important furfural derivatives, such as furfuryl alcohol, tetra hydro furfuryl alcohol, acetyl furane, furoic acid, methyl furane and tetrahydrofuran THF are identified. Current world production of furfural is about 250,000 t/a, at a stable price of $1,000/t; and it is being projected to 225 thousand metric tons per annum.

Keywords: *Batch process, cellulose, continuous processes, corn cobs, fixed-bed reactors, oat hulls, pentosans, rice hulls, sugar cane bagasse, Quaker Oats technology.*

Introduction

Furfural[1] is produced from agricultural waste biomass that contain pentosans, which are aldose[2] sugars, composed of small rings formed from short five-member chains, that constitute a class of complex carbohydrates, present in cellulose of many woody plants such as corn cobs, sugar cane bagasse, rice and oat hulls etc. (Brady, *et al.* 2000). Furfural is a clear, colorless motile liquid with a characteristic 'almond-benzaldehyde' odor. The molecular formula is $C_5H_4O_2$. Its synonyms are: 2-furancarboxaldehyde, furaldehyde, 2-furanaldehyde, 2-furfuraldehyde, fural, furfurol.

When exposed to sunlight in the presence of oxygen auto-oxidation occurs and it darkens to a dark red/brown color (Brenkem Consultants Asia Co. 2004).

In theory, any material containing pentosans can be used for the production of furfural. Technically furfural is produced by acid hydrolysis of the pentosan contained in woody biomass. Almost all furfural plants employing the *batch process* use the Quaker Oats technology developed in the 1920's. They all operate at less than 50% yield, needs a lot of steam and generate plenty of effluent waste. Moreover their operating costs are high. Hence such plants throughout the world are closing, with the exception of simple low cost Chinese plants (Dalin Yebo Trading 2004).

Some have resorted to *continuous processes*. Westpro modified Chinese Huaxia Furfural Technology is an example of a leading current continuous process furfural technology (Westpro 2004). It uses fixed-bed reactors and continuous dynamic refining, which gives high yields of furfural, including byproducts, at low production costs. The technology requires only low capital investment and is thus especially suited for developing countries, and also for relatively poor communities that are facing economic difficulties, such as refugees displaced across their national borders into neighboring countries where agriculture thrives.

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[1] The International Union of Pure and Applied Chemists (IUPAC) names for aldehydes end in –al. Hence furfural has an aldehyde – CHO functional group (McMurray and Fay 2004).

[2] Sugars that contain aldehyde functional groups. The word aldose is a combination of two words: -ald stands for aldehyde and -ose stands for sugars. Names of sugars end in –ose. Examples are glucose, fructose, sucrose (McMurray and Fay 2004).

For example the capital for equipment is only $500,000 for a furfural plant with an annual capacity of one thousand metric tons. The typical size of plants using this technology is 500 ~ 6000 metric ton furfural per annum. About twenty personnel are sufficient to operate the plant, and the land requirement is only about 5,000 m^2. The expected annual profit before taxes is estimated to be between US$ 1 and 2 million (Westpro 2004). Furfural is the only organic compound derived from biomass that can replace the crude oil based organics used in industry (Dalin Yebo Trading 2004).

Most furfural plants are located close to available raw materials. Dictated by the harvest of agricultural products, most plants operate on a 7-8 month schedule.

Downstream products include furfuryl alcohol, tetra hydro furfuryl alcohol, acetyl furane, furoic acid, methyl furane and tetrahydrofuran THF (Brenkem Consultants Asia Co. 2004). Furfuryl alcohol, used mainly in the production of furan resins for foundry sand binders, is the major market for furfural. It is also widely used industrially as a refining solvent in the manufacture of synthetic rubber. Furfural can be used for the production of lubricants; specialist adhesives and plastics; and nylons. It is the starting material for cycling shorts (Hebei Furan Chemical Economic & Trade Ltd. 2004).

World production of furfural shifted from developed countries to developing countries during the early 1990s. Western European production was significantly reduced, while Chinese production increased. At present the largest producers of furfural are China and the Central Romana Corporation in the Dominican Republic (see Table 1). In China furfural is produced from corncobs in the northern provinces. Many small plants and several large ones exist, particularly in Shandong Province (Brenkem Consultants Asia Co. 2004). Over the next five years Chinese production of furfural and furfuryl alcohol is projected to increase at an average annual rate of 5% provided no shortage of raw material (corncobs) is experienced. China is the only major region where increased furfural production is expected in the next five years.

Current world production is *ca.* 250,000 t/a; and the price is usually static at $1,000/t. The world operating capacity is estimated to be approaching 225 thousand metric tons per year (SRI Consulting, 2004).

World furfural consumption is shown in table 2. U.S. consumption of furfural is expected to stabilize at an average annual rate of 2.0% over the next five years. Restructuring, de-emphasis, plant closures and inexpensive furfural imports from China and the Dominican Republic have prompted the closure of many U.S. plants. Four furfural plants were shut down in the United States between 1995 and 2003, causing an annual capacity loss of 90 thousand metric tons. Currently there is only one U.S. producer, Quaker Oats-Pepsico, which uses oat by-products to make furfural.

European overall consumption of furfural remained constant at over 40 thousand metric tons from 1996 to 2000. Japanese furfural consumption declined to about 2.5 thousand metric tons in 2000. The largest furfural market used to be for furfuryl alcohol production. But the largest market now is lube oil refining. Little or no growth is projected to 2005 (Levy and Yokose 2004).

Westpro Modified Huaxia Technology

The Chinese Huaxia Furfural Technology uses fixed-bed reactors and continuous dynamic refining, and gives a high yield of furfural and byproducts at a low production cost. It is a popular example of a *continuous process* that has replaced the less efficient *batch processes*, which characteristically gives yields of about 50% only. The process was modified by Westpro (2004).

The steps involved are pretreatment, hydrolysis, refining and byproduct recovery. Technical details are mentioned below. The hydrolysis step, developed in 1970s, was modified in the 1980s with the use of controlled electrical discharge components. The refining process and byproduct recovery, developed in 1980s, has been continuously improved by using advanced US control technology.

This greatly improved byproduct yield, especially acetic acid recovery. Most furfural made by other technologies in U.S. or European is only 98 % in purity; but Westpro Huaxia's Technology yields 98.5 - 99.5% furfural.

The capital investment for a new furfural plant is only one third that of other furfural technologies.

In this furfural process, acetic acid, a valuable byproduct, can be recovered. Another byproduct, levulinic acid may be obtained with acid refining equipment. Hydrogenation of furfural yields furfuryl alcohol, which is a value added product that has a broad world market.

The Technical Process

Westpro modified Huaxia technology includes pretreatment, hydrolysis and refining processes.

Pretreatment

The pretreatment equipment depends on the raw materials used. Corncobs are usually crushed to 3 ~ 10mm before blending with sulfuric acid.

Hydrolysis

The pretreated raw materials are charged to steel rectors or digesters, which are lined with acid proof cement carbon bricks. The furfural formed is removed with steam. The furfural-saturated steam is filtered to remove solid particles and condensed by cooling down to about 60^{o}C. Two recovery towers may be added for acetic acid recovery. To save cooling water and energy, a secondary steam generator may be used for distillation. A cooling tower may also be introduced to recycling water.

The condensed furfural solution is then fed to the furfural azeotropic distillation column. The condensate is separated into two fractions. The light water phase is refluxed and the heavy furfural phase undergoes refining by azeotropic distillation. The furfural layer has about 6 % water, some light fractions, and a small amount of acid, which is neutralized by sodium carbonate prior to refining. The wastewater at the bottom of the azeotropic column contains 1% acetic acid that can be neutralized or recovered as acetic acid.

Refining

A continuous dynamic azeotropic distillation is used. The furfural layer is fed continuously from the top of a refining tower. The light fractions, like acetone and methanol, are removed from the top as byproducts. At the end of the feed distillates are collected in storage tanks under a vacuum at various reflux ratios. The system is computer controlled. This dynamic distillation has many advantages, such as equipment and energy efficient, byproduct recovery, high refining yield and high product quality. The quality can be varied from 98.5 to 99 % or even higher by changing computer control parameters.

Further hydrolyzation of the biomass residue after furfural production, under a higher reactor temperature, yields levulinic acid, which is then refined by extraction and vacuum distillation. Furfuryl alcohol may be obtained by hydrogenation.

Equipment

List of required key equipment

1. pretreatment equipment (a crusher for corn cobs, or a rotary dryer for wet bagasse)
2. acid blender
3. reactors
4. filters
5. secondary steam generator
6. azeotropic distillation tower
7. refining tower with digital control parts
8. control panel
9. computer with data acquisition and control software.
10. two vacuum pumps
11. liquid pumps tanks, piping, gauges, etc
12. Options: boilers, water treatment, cooling tower, acetic acid recovery equipment.

Raw Material

Typical furfural yields from various raw materials by using Huaxia Furfural Technology are the following:

1. Corn cobs: 10~12 %
2. Rice hulls: 5.0 ~ 7 %
3. Flax dregs: 5~7 %
4. Cotton hulls: 8~11 %
5. Sugar cane bagasse: 8~11 %
6. Wood: 4~8 %

Furfural yields depend on the pentosan content. Humidity also affects furfural yield.

Operation

Plant Feeds (per ton of furfural):

1. Power: 200~600 KWh;
2. Steam (8~14 kg/cm2): 25~35 tons, depends on byproduct options.
3. Cooling Water: 30~50 tons, depends on byproduct options.
4. Sulfuric acid: 0.3~0.8 ton, depends on raw materials.
5. Sodium carbonate: 0.01 ton
6. lime: ~0.5 ton (or limestone 1 ton), or none if recovering acetic acid .

Byproducts

Yield per ton of furfural is shown below. The values are dependent on raw materials and can vary.

1. Methyl alcohol: 0.15~0.175 ton
2. Acetone: 0.15~0.175 ton
3. Acetic acid: 0.45~0.8 ton

Operation Staff:

1. Raw material pretreatment: 0~3 (0~1 in each of three shifts)
2. Hydrolysis: 6~9 (2~3 in each of three shifts)
3. Refining:1~2 (1~2 in each of one shift)
4. Recovery of lights:1~2 (1~2 in one shift)
5. Acetic acid recovery: 3 (1 in each of three shifts)
6. Analysis and quality control: 1 in one shift
7. Chemical Engineer: 1~2
8. Plant manager 1
9. Subtotal: 10~23, depending on options and the size of the plant.
10. Other: 3~6 (1~2 in each of three shifts)

Recommended Land Area

1. Furfural Process: 1510 sq. meters
2.Boilers and water treatment: 6m x 10m
3.Raw material storage: 500~2000 sq. meters
4.Office, road and other: 200~500 sq. meters

Economic Considerations

Economic evaluation of a typical 1500 metric-ton/year furfural plant

Furfural produced at 1500 MT/Yr with the market price of $ 1700/ton but selling at $900/ton yields $1350,000.

Methyl Alcohol produced at 250 MT/Yr with the market price of $ 250/ton but selling at $100/ton yields $250,000.

Acetone produced at 250 MT/Yr with the market price of $ 800/ton but selling at $400/ton yields $100,000.

Acetic Acid produced at 800 MT/Yr with the market price of $ 900/ton but selling at $700/ton yields $560,000.

This brings the Total sales/year to $2,030,000

To this may be added Levulinic acid production at 2000 ton/yr making an additional $2,000,000. Also furfuryl alcohol production at 1500 ton/yr will bring another $1,500,000.

The total cost per year (at $300~450 /ton furfural) is $600,000. The projected profit before taxes is therefore $1-2 million.

The capital investment for equipment plus boilers is $1,500,000 and the capital for building, land etc. will be between $ 300,000 and $ 800,000. Annual furfural pricing is shown in Table 3.

Current Uses of Furfural

(a) As Furfural. Recovery of lubricants from cracked crude. Solvent extraction. Pine oils etc. Specialist adhesives. [Russia]. Flavor compound. [Europe]

(b) As 5-Methyl Furfural. High value flavor compound.

(c) As Furfuryl Alcohol. $C_5 H_6O_2$ Synonyms are FA, 2-Furanmethanol, furylcarbinol, and 2-hydroxymethylfuran. Characteristic features are: colorless or straw colored water like liquid with a bitter taste and chrematistic odor. Flammable, soluble in water and darkens on exposure to air. On addition of organic and/or inorganic acids, reacts explosively producing intense heat.

It is used in the production of furane resin, surface coatings, pharmaceuticals, mortar, specialty polymers, chemically resistant resin, etc., boiler and floor grouting, adhesives used in foundry cores and moulds.

High interest is evident in a paper where three binder suppliers - Ashland Specialty Chemical Co., Dublin, Ohio; HA International, LLC, Westchester, Illinois; and Hormel Foods Corp., Austin**,** Minnesota - forecast how their core binders will adapt to meet the future demands of environmental regulations, extended shelf life and tighter dimensional accuracy facing the metal casting industry (Tackes 2001).

(d) As tetrahydrofurfuryl alcohol. Widely used precursor for specialty chemicals. Used as a binder in catalyst for the new pebble bed reactors (Crandell 2003).

(e) As tetrahydrofuran [THF]. Precursor for wide range of chemical syntheses (BASF. 2002; Penn Specialty 2001). Starting material for PTMEG. [Polymeg / Spandex].

Other Opportunities

As furfural has unique properties a host of opportunities are available provided the production cost can be reduced. Drug and specialty chemical manufacture; replacement of phenol in foundry resins; and specialized polymers are some possibilities. For example, di-furfural is stronger than other high strength polymers.

A derivative of current interest is tetrahydro-2-furanmethanol (THFA) - $C_4H_7OCH_20H$. It is a transparent motile liquid with characteristic odor. It is being developed as a solvent for cleaning electronic components; as chemical coupling agent in organic syntheses; and making vinyl resin, dyes, and rubber. (Brenkem Consultants Asia Co Ltd, 2004).

Conclusion

Furfural is a utility chemical. The manufacture is simple, the raw material is agriculture waste, the capital is reasonable and within reach of many small communities. Thus furfural may aptly be dubbed “Gold from Garbage”

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FF Production		
Country	**Principal Feedstock**	**Production (tpa)**
China	Corncobs	200,000
Thailand	Corncobs	8,500
Dominican Republic	Bagasse	32,000
South Africa	Bagasse	20,000
Spain	Corncobs	6,000
Others (Incl. India & South America)	Corncobs/Bagasse	<15,000
Russia (used internally, only)	Corncobs	unknown
Total		**>280,000**

Table 1. World Furfural Production

FF Consumption			
Country/Continent	**Sales (tpa)**		
	Furfural	**PTMEG & Others**	**Furfuryl Alcohol**
Europe	12,000		7,000
USA	8,000	20,000	20,000
Middle East	7,000		
Japan	6,000		15,000
Taiwan	5,000		5,000
South America	5,000		10,000
China	5,000		6,000
Australia/Souh Africa	2,000		6,000
UK			12,000
Germany			18,000
Others	up to 50,000		31,000
Subtotal	**50,000 - 100,000**	**20,000**	**130,000**
Total	**200,000 - 250,000**		

Table 2. World Furfural Consumption

FF Pricing			
Date	**Price Range ($/t)**		**Comments**
1995	675	1,250	Drought in China
1996	840	1,845	Drought in China
1997	860	1,225	Drought in China
1998	830	990	
1999	690	865	
2000	630	705	
2001	>650		
2002	500	1,100	

Table 3. World Furfural Pricing 1995 - 2002