

SAIChE GOLD MEDAL

BACKGROUND INFORMATION SUPPORTING THE NOMINATION

THE SUPRAYIELD® PROCESS FOR FURFURAL PRODUCTION

Overview

A small group of three Chemical Engineers and a Chemist have developed, patented and licensed a new process for the production of furfural. The novelty of the development stems from the recognition that all processes to produce furfural worldwide have fundamental weaknesses which the team have explained by detailed analysis of thermodynamics and mass transfer. The patented SupraYield® process operates at elevated temperature and pressure, resulting in shorter reaction times and lower energy consumption. It employs decompression as a means of vaporising furfural, rather than the traditional steam stripping. As a result, all process efficiency indicators are greatly improved, especially purity and steam consumption.

Furfural is produced by catalytic dehydration of pentose, which is obtained by liquid phase acid-catalysed hydrolysis of pentosan polymers in woody, usually waste, vegetable matter. Current traditional industrial furfural processes strip furfural from the woody substrate using live steam. The SupraYield® process overcomes problems of energy inefficiency, yield-loss, product purity and effluent generation by using adiabatic flash distillation in the reactor.

SupraYield® is a cost-effective technology. It reduces CAPEX and OPEX with the production costs reduced from about US\$ 550-700/t to US\$ 250/t. In addition to the reduced CAPEX, IRRs are well in excess of 30%, depending on the feedstock used.

The first technology licence agreement has been concluded with Proserpine Co-operate Sugar Milling Association Limited, north of Mackay, Queensland, Australia, for the construction of a five-thousand tonne/yr plant for start-up during second quarter of 2005.

The development work and industrialisation of the technology is the result of a partnership between Durban-based International Furan Technology (Pty) Ltd and the University of KwaZulu-Natal School of Chemical Engineering.

Furfural Manufacture and Use

Furfural has been made from agricultural waste products since the 1920's and is one of the few bio-based chemicals that compete with crude oil. It was used as a precursor for Spandex (Lycra®) until 2001, and now finds application as furfuryl alcohol in foundry resins, in the production of lubricating oils and as a process chemical. In 2002 furfural

was registered in South Africa (registration number L6864) and Spain, etc., as a nematicide, to replace methyl bromide, carbamates and phosphorus-based chemicals, all of which are under threat due to environmental considerations. Recently, a wood-treatment process has been formulated on the basis of furfural alcohol which will replace the toxic treatment of wood with copper-chrome-arsenate (CCA). This treatment process has been further modified to turn e.g. birch into a product with tropical wood qualities (visual and texture), which has been accepted in the Scandinavian markets as a true alternative to tropical hardwoods. Furfural and other furans are under test as components of biodiesel.

Furfural is produced by the acid hydrolysis of the pentosan in woody vegetable waste products such as bagasse, corncobs, corn stover, wood chips and oilseed husks and stalks. Presently the only furfural production technology offered for sale and commercial use is the Chinese batch process (Westpro 2004) which is inefficient and achieves yields around 30 to 40% of theoretical with a reactor residence time of 4½ to 5½ hours, a steam usage of 50t per t of furfural and an effluent stream containing 1.2% m/m acetic acid. This means that in the developed world there is no environmentally acceptable furfural process technology available that meets normal financial criteria. Since the market for furfural is expanding and perceived to continue to do so, a process with the SupraYield® advantages finds a natural application.

The reaction sequence taking place is a simple hydrolysis of the pentosan polymers (e.g. xylan) to the pentoses (e.g. xylose) followed by catalytic dehydration to form furfural. Yield-loss reactions occur while the furfural is in the liquid phase, by polymerisation and by reaction with the precursor pentose, accounting for the low yield figure achieved in traditional processes.

All currently used furfural production processes worldwide strip the furfural from the biomass substrate using live steam. This is inefficient because the diffusion of furfural through the liquid surrounding and within the solid substrate into the stripping steam is slow. This high furfural residence time in the liquid phase allows yield-loss reactions to occur. In addition, by-products such as alcohols, acetic and formic acid, 5-methyl furfural and furyl methyl ketone that form due to side-reactions also diffuse and are stripped out of the substrate to contaminate the final product and need to be disposed of as effluent. The SupraYield® process overcomes these problems, producing furfural that is virtually free of these by-products and effluents.

Background Theory

The standard analytical method for the quantitative determination of pentosans in woody material (TAPPI 1984) is based on conversion to furfural and has a pentosan-to-furfural yield of 100% on a molar basis. The procedure consists of an atmospheric digestion in 13.5% m/m aqueous hydrochloric acid saturated with sodium chloride. The reaction medium is boiled continuously at 110°C, and furfural, immediately on being produced, leaves the liquid phase and enters the vapour phase and is withdrawn from the reaction flask. The vapour is then condensed and the condensate is analysed for furfural, which is

then related back to the pentosan content of the woody material. If the furfural, on creation, were to remain in the liquid phase it would be susceptible to yield-loss which would render the analytical process useless. This unwanted residence time in the liquid phase is the major reason why the current industrial processes give poor yields in comparison to the TAPPI method.

The principal reactions by which furfural is formed are shown in Figure 1. However, side-reactions occur in the liquid phase and reduce the furfural yield. These are shown in Figure 2. Although the analytical method is contrived to avoid the side reactions, the existing industrial production processes are not. Indeed, it seems to us that they are, unfortunately, designed to encourage them through long residence times (5hr) and low temperatures.

No current industrial processes vapourise the furfural as it is formed. Instead, furfural remains in the liquid phase surrounding, or being an integral part of, the woody raw material for a certain period of time. This residence time is caused by the need to allow the furfural to diffuse through the particle to the surface where it is then available to be stripped by steam. During this time the furfural molecule reacts with its precursor, pentose, or indeed another molecule of furfural to eventually form a polymer, as shown in Figure 2.

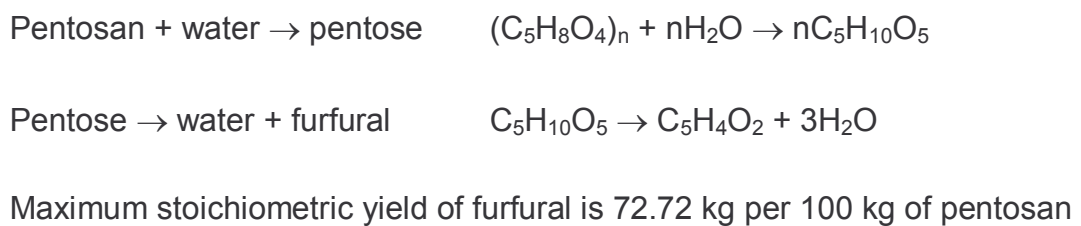


Figure 1 reactions producing furfural

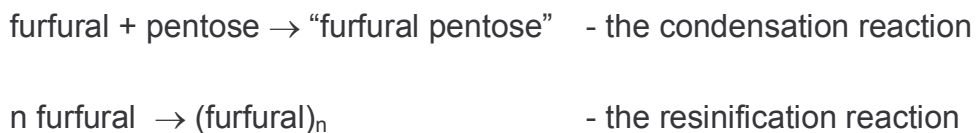


Figure 2 reactions destroying furfural

Thermodynamics

Traditionally, after reaction, when stripping steam is passing through the bed of wet solid substrate, the liquid phase present within the solid, a solution of pentose and furfural etc.,

cannot be heated to its bubble-point temperature with saturated steam. This is due to reduced water activity as expressed by the well-known phenomenon of boiling-point rise. Consider the phase diagram shown as Figure 3. This shows the furfural/water system represented by a plot of furfural concentration as a function of temperature for furfural in an aqueous solution. The upper vapour/liquid envelope represents the situation encountered in the TAPPI analytical method. Boiling occurs at 110°C (13.5% hydrochloric acid saturated with sodium chloride) when the furfural concentration is zero. The lower vapour/liquid envelope represents the situation encountered in a traditional furfural plant, where the typical concentration of pentose is 1% m/m in the solution surrounding the solid particles. Boiling occurs at 102°C.

If a small furfural concentration, X, is generated (by reaction) in the first system representing the analytical method, this leads to a point lying in the vapour part of the phase diagram shown as Y. This means that any furfural formed in this boiling solution will be instantly transferred to the vapour phase where it cannot react with pentose or itself since neither pentose nor the acid catalyst are volatile. Consequently, in this case, yield-loss reactions between furfural and pentose and between furfural and furfural are not possible, leading to the yield of 100%. On the other hand, if a small furfural concentration X is generated in the second system, being heated by condensing steam at atmospheric pressure, this leads to a point Z lying in the liquid part of the diagram. Hence in the present industrial furfural reactors the reaction medium is not brought to the bubble-point and furfural remaining in solution can react to form by products as mentioned earlier. Entrainment of furfural vapour by stripping steam is a slow and inefficient process allowing ample time for yield-loss reactions to take place. Furthermore, and most significantly, the stripping of other side-reaction products occurs, leading to product contamination and therefore larger separation and purification steps downstream.

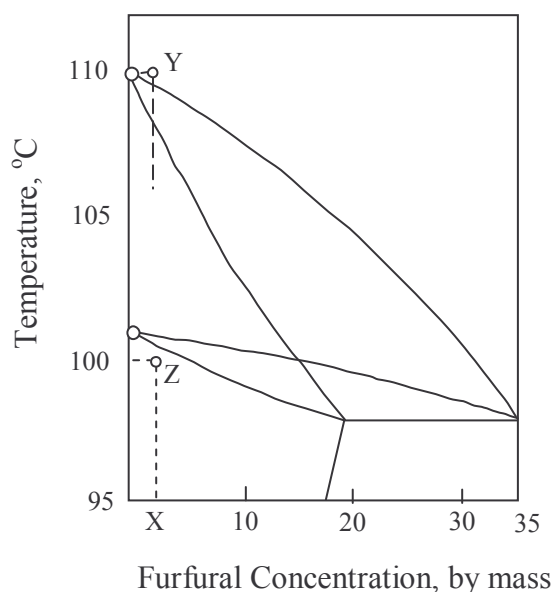


Figure 3 The furfural/water phase diagram (illustrative) from Zeitsch (2000)

If the industrial process could be construed so as to mimic the analytical process then yields would be increased from around 40% to around 100%. The difficulty, of course, in an industrial reactor, is to cause boiling to take place in a liquid absorbed on a bed of particulate solids that have thermal properties more resembling an insulator than a conductor. The solution is to reduce the pressure.

In the SupraYield® process the reactions occur at elevated pressure and temperature, around 15-30 bar and 200-235°C. After a short time, of the order of a few minutes, the reactor is depressurised slowly and vapour leaving the reactor is condensed, and subsequently purified in the conventional manner.

This gradual depressurisation can be controlled so that the rate of vapourisation is matched to the rate of production of furfural, minimising the retention time of furfural in the liquid phase. In addition, any components present in the liquid phase which have a volatility significantly lower than furfural will tend to be retained in the liquid phase. Acetic and formic acids are such components.

Reaction kinetics

The hydrolysis of pentosan followed by the formation of furfural are sequential reactions whose rates have been shown to be dependent on the hydrogen ion concentration, the concentration of reactant and the temperature, according to several investigators. Dunning and Lathrop (1945) treated corncobs with sulphuric acid at 1,9% and 4,4% to obtain a rate constant for the formation of pentose from pentosan, confirming earlier data on the similar reaction occurring in oathulls (Bryner et. al., 1936). Under conditions approximating to the expected temperatures in a furfural reactor, Root et. al. (1959) obtained a rate constant for the disappearance of pentose. Of course, conversion of pentose is equal to yield of furfural only if side reactions are negligible. It was assumed, under the conditions prevailing, that the side reactions were indeed negligible. The applicable rate equations were applied to the conditions in the proposed reactor and conversions to furfural were calculated.

The assumed reaction sequence is:



giving the well-known equation

$$\frac{dC_{pe}}{dt} = k_0 C_{pn} - k_1 C_{pe} \quad (2)$$

where C refers to the concentration in g/l and pe denotes pentose and pn pentosan.

k_0 is the rate constant for the formation of pentose

and k_1 is the rate constant for the formation of furfural.

From the work of Dunning (1945) and Bryner (1936), as quoted by Zeitsch (2000), the expressions for the dependence of the rate constant on temperature are:

$$k_0 = 7.832 \times 10^4 C_H e^{\frac{-5163}{T}} \quad (3)$$

$$k_1 = 9.306 \times 10^{15} C_H C_{pe} e^{\frac{-16894}{T}} \quad (4)$$

where C_H is the hydrogen ion concentration (g/l) at 20°C.

C_{pe} is the pentose concentration (g/l)

T is the absolute temperature

The following equations for the concentration variation with time were adapted from Levenspiel (1972):

$$C_{pn} = C_{pn_0} e^{-k_0 t} \quad (5)$$

$$C_{pe} = c_{pn_0} \left[\left(\frac{e^{k_0 t}}{(k_1 - k_0)} \right) + \left(\frac{e^{-k_1 t}}{(k_0 - k_1)} \right) \right] \quad (6)$$

$$C_{ff} = C_{pn_0} \left[1 + \left(\frac{k_1}{k_0 - k_1} \right) e^{-k_0 t} + \left(\frac{k_0}{k_1 - k_0} \right) e^{-k_1 t} \right] \quad (7)$$

Conveniently, even though the rate constants were determined under laboratory conditions, the predicted batch conversions were found to be comparable to those experienced personally on a variety of actual plants.

At 206°C the predicted concentration profiles of pentosan, pentose and furfural are shown as a function of time with, 3% sulphuric acid as catalyst, in Figure 5. These profiles are consistent with the predictions of Zeitsch (2000).

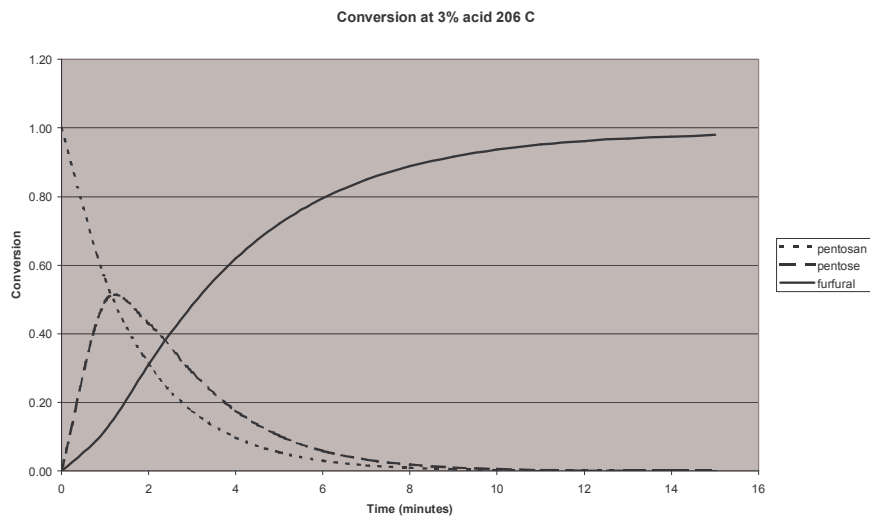


Figure 5 The predicted conversion of pentosan to furfural

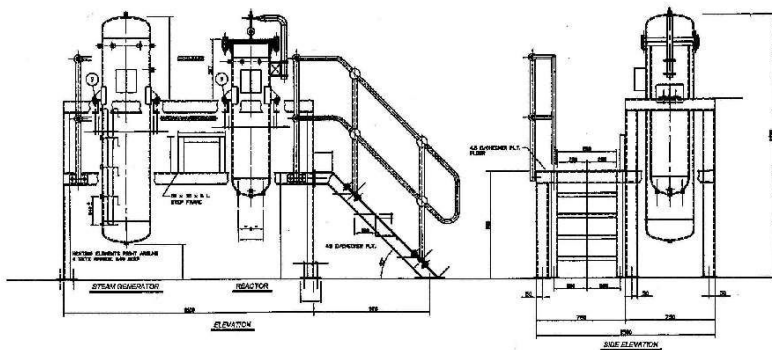
Acid concentration has a major influence on conversion. The predicted conversion in figure 5 was based on hydrogen ion concentration at 20°C. At elevated temperatures the ionisation of aqueous solutions of mineral acids reduces significantly, as a consequence of the reducing dielectric constant of water (Franck et al 1956). Thus the actual hydrogen ion concentration, using sulphuric and phosphoric acid as examples, reduces by a factor of 0.36 between 20°C and 206°C, whereas for hydrochloric acid the factor is only 0.13 (Noyes et al 1909). Care was thus taken to use kinetic data from experimental work using the identical acid, rather than relying on the hydrogen ion concentration (irrespective of the acid) at ambient temperature.

Experimental work

In 1999 a small 0,3l laboratory-scale test rig was constructed to verify the elementary design principles. This consisted of a cylindrical reactor connected to a 300l steam generator designed to supply a small steam flow at a pressure of 4MPa. 100g of raw material was placed in the pre-heated reactor as a fixed bed, the lid closed and the steam admitted. After allowing a few minutes for reaction to start, the pressure was slowly reduced via a small orifice plate, and the resulting exit vapour was condensed at atmospheric pressure. The condensate was collected, weighed and analysed for furfural content. Although the results of this phase of the work are not reported here, there was sufficient confidence in the SupraYield® process to proceed to pilot scale.

The fixed bed pilot plant

To prove the process on a semi-industrial scale, a pilot plant was designed and built in the School of Chemical Engineering at the University of KwaZulu-Natal. It consists essentially of two pressure vessels, a 40 atm. lagged steam generator fitted with 60 kW external electric elements and an 80l lagged 30 atm fixed bed pressure reactor. The steam generator is connected to the reactor by a steam transfer pipe and double isolating valves. The reactor has an opening lid to charge solid raw



SupraYield® - Pilot Plant (80 l)

material. Internally it has a basket to suspend the solids in the steam, which is supplied batch-wise from the steam generator. A micro-orifice plate and simple valve system is attached to the reactor for depressurisation.

Depressurised vapours

are led from the reactor to a simple immersion condenser, a dephlegmator and a collection vessel. Both pressure vessels are fully instrumented and fitted with safety devices.

Operating Procedure

The steam generator was filled to the specified level with cold tap water. The electric elements were switched on and the pressure was allowed to reach 40 atm.

The reactor lid was tightened down and steam from the generator pressurised the empty reactor. This was done to pre-heat the reactor so that the amount of condensate generated during the actual reaction phase was minimised. The reactor pressure was allowed to reach 30 atm. and was maintained over a period of about two hours. The reactor was depressurised using the bottom outlet valve and the top lid was removed, the solids charged, the lid replaced and the reactor repressurised to the specified value.

After a short holding time the reactor was slowly depressurised. Furfural produced during the holding time condensed along with water in the condenser and flowed through the dephlegmator into the collection vessel. The rate of depressurisation was controlled, and measured by noting the volume of condensate produced over a short period of time.

When the concentration of furfural in the condensate fell to a specified value, the outlet was closed and the reactor allowed to cool overnight. It was then opened up and the solids discharged and set aside for further examination. The furfural-rich condensate separated into two phases during part of the time that it flowed from the reactor. These phases were subsequently measured and analysed.



Fixed bed pilot plant (2001)

Results and discussion

Over 200 test runs have been done so far on the fixed bed reactor, using a wide variety of feedstocks. Yields have increased consistently and are now over 80%. The results of a run performed as a witnessed verification run are given here.

Feedstock

| | |
|----------------------|------------------------------|
| Type of feedstock | Sunflower husks |
| Weight of the charge | 3636 g |
| Moisture Content | 14.8% |
| Pentosan Content | 20.2% dry basis. |
| Acid added | 260ml of 50% orthophosphoric |

Heat up cycle

| | |
|---|-------------------|
| De-aeration | 4 minutes |
| Temperature stabilisation | 4 minutes @ 165°C |
| Time needed to heat from 165°C to 210°C | 3 minutes. |
| Operating Temperature Range | 210°C to 200°C |

Condensate was collected into receivers which were sampled and analysed for furfural concentration by refractive index. In four of the receivers the furfural concentration was greater than the solubility in water, forming two phases which separated immediately. The lower phase was a saturated solution of water in furfural and the upper a saturated solution of furfural in water. This is the first production of a furfural stream in an industrial reactor which has a concentration high enough to separate into two layers. The azeotrope of furfural and water is heterogeneous at room temperature. All solutions were clear, with no suspended solids.

Samples of the bulked material were analysed by gas chromatograph to confirm the refractometer results.

A sample was analysed for contaminants and by-products using a gas chromatograph with a mass-selective detector. Traces of acetaldehyde, methanol and ethanol were found (collectively called "light ends") and a small quantity of 5-methyl furfural and acetic acid was present. The calculated yield of furfural on pentosan was 78% of the theoretical maximum, or 97kg of pure furfural per tonne of husks as received.

The rate of depressurisation of the reactor was found to be a key operating variable as it controls the rate of boiling and the rate of emission of vapour phase furfural from the reactor as it is formed. The rate of decompression also determines the cycle time of the reactor. It would be most desirable to alter the depressurisation rate within the run as an optimisation procedure matching the furfural produced. The depressurisation rates quoted here were constant over the entire run.

Compared to other processes, the new SupraYield® process has distinct advantages, as summarised briefly in Tables 1 and 2.

Table 1 - the comparison of the SupraYield® process to the conventional

| | Chinese Batch Process | SupraYield® Process |
|---|------------------------------|----------------------------|
| Yield (typical) % | 35 | >60 |
| Typical Reactor Residence Time (minutes) | 270 | 75 |
| Specific reactor output for 15% moisture content corn cobs - kg furfural / m³ reactor/h | 2.0 | 10.8 |
| Furfural concentration in distillation feed (wt %) | 2.5 | 10 to 14 |
| Steam Consumption (t/t Furfural) | 50 | 10 |

TABLE 2 – Breakdown of Production Costs

| Cost Factors US\$/t FF (excl. depreciation) | Chinese Designed Plant | SupraYield® Plant |
|--|--------------------------------------|---------------------------------------|
| | 30% Yield Steam usage (55 t/t FF) | >60% Yield Steam usage (10 t/t FF) |
| Relative Cost of: | | |
| - Corncobs | 210 | 126 |
| - Labour | 80 | 15 |
| - Maintenance | 28 | 5.5 |
| - Effluent & Steam | 163 | 44 |
| Contingency 30% | 134 | 57.5 |
| | \$615/t | \$248/t |

Conclusions

1. The SupraYield® process produces furfural from sunflower husks, bagasse, rice hulls, corn cobs and stover, wood chips and probably all pentosan-containing agricultural materials.
2. The yield of furfural is around 60% of theoretical, depending on the raw material and the selected process conditions. This is almost twice the yield obtained in most plants operating today.
3. Contamination levels are low, as much as an order of magnitude lower than conventional plants.
4. The effluent produced by the SupraYield® process is much lower in quantity than existing processes.
5. Steam consumption is up to ten times lower.
6. Reduced residence time / reactor volume at 6% of current processes.

7. Simplified plant design and operation.
8. Most importantly, the SupraYield® process represents a major step forward in the efficient use of biomass to produce a range of chemicals, and has been accepted internationally as setting new standards in efficiency and cost.

Current work

Extensive testwork is underway with a moving bed reactor, perceived to have inherent process advantages over the process described above.

References

- Bryner, C., Christensen, L.M. and Fulmer, E.I., Ind. Eng. Chem. 28 (1936) 206-208)
- Dunning, W and Lathrop, E C Ind. Eng. Chem. 37 (1945) 24-29
- Levenspiel, O., Chemical reaction engineering, Wiley (1972)
- SA Patent (2001/6721) and international patent applications/patents as a result of PCT/ZA00/00024
- TAPPI Test methods, test no. T223 cm -84 "Pentosans in wood and pulp" (1984)
- DalinYebo: www.dalinyebo.co.za/dyT (May 11, 2004)
- Westpro: www.westprochem.com (May 11 2004)
- Zeitsch, K.J. The chemistry and technology of furfural and its many by-products, Elsevier, (2000)

Lycra® is a registered trademark of Du Pont

SupraYield® is a registered tradename of International Furan Technology (Pty) Ltd
(www.ift.co.za)