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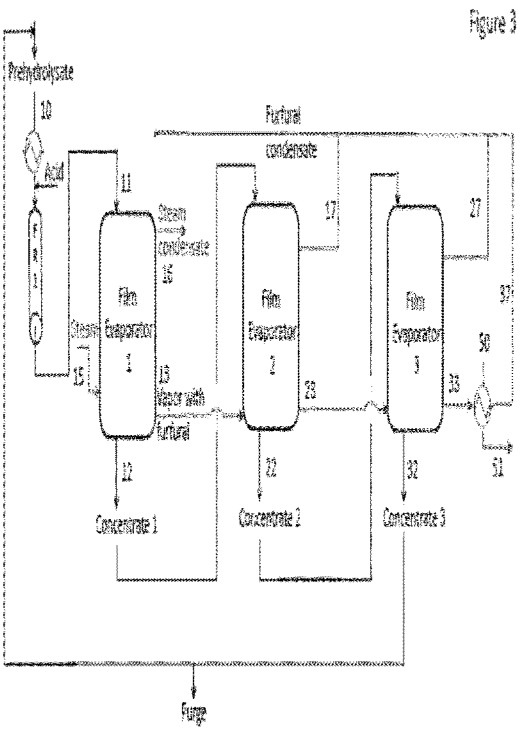

(57) Abstract: This invention relates to a method for producing furfural from a pentose or pentosan-containing starting material, in a pressurised continuous flow reactor followed by one or more reaction vessels, wherein the one reaction vessel is a film evaporator or wherein at least one of the more than one reaction vessels is a film evaporator; and wherein the pentose or pentosan-containing starting material is brought as a liquid stream into the pressurised continuous flow reactor.

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A method for producing furfural

Field of the Invention

This invention relates to a method for producing furfural from a pentose or pentosan-containing starting material.

Background of the Invention

With the diminishing supply of crude oil, the use of renewable energy sources is becoming increasingly important as a feedstock for the production of hydrocarbon compounds. Plants and animal biomass are being used to produce liquid and gaseous hydrocarbon compounds. One of the advantages of using biomass is that the CO_2 balance is more favourable when compared with conventional hydrocarbon feedstock.

One of the most commonly used biomass material is a pentose or pentosan-containing starting material that is lignocellulosic biomass material. Lignocellulosic biomass materials primarily consist of cellulose, hemicellulose, and lignin bonded together in a complex structure along with optional small quantities of extractives, pectins, proteins, and/or other materials.

The pentose sugars in hemicellulose present in the lignocellulosic biomass material can be processed to obtain pentose sugars which can later be converted to fuels and chemicals, such as furfural~~s~~. Furfural has various applications in the chemical and petrochemical industry and the derivatives of furfural are also useful as polymers and resins.

Furfural (also known as furan-2-carboxaldehyde, fural, furfuraldehyde, 2-furaldehyde, or pyromucic aldehyde) is a product of the dehydration of 5-carbon sugars, and may be obtained by the acid catalyzed dehydration of 5-carbon sugars (pentoses), particularly xylose:

$$C_5H_{10}O_5 \rightarrow C_5H_4O_2 + 3\ H_2O$$

Pentoses may be obtained from pentosans that are, in turn, obtained from hemicellulose present in lignocellulosic biomass.

A multi-effect evaporator can be used to evaporate water. In a multiple-effect evaporator, vapour from one body heats a second body at a lower boiling temperature. The first effect is heated directly with steam, and the additional bodies are ordered based on descending boiling temperature (or pressure). Multiple effect evaporation is commonly applied to improve the energy efficiency of evaporation and known by those skilled in the art. WO2006095340, for example, discloses a plurality of evaporators connected in series. In each successive evaporator, more water is distilled off. However, no chemical reaction occurs within each evaporator.

EP 0124507B1 produces furfural from diluted aqueous solution in a series of reactors, each reactor operating at a different temperature and pressure, while recovering the furfural partially in the condensate. This condensate is formed by flashing of part of the liquid entering a downstream reactor as this downstream reactor is operating at lower temperature and pressure than the upstream reactor. In EP 0124507B1, the total amount of vapour produced is limited by the temperature difference between the first and last reactor in the series. As no evaporation takes place in the reactor, the majority of the produced furfural will remain in the liquid phase of the reactors, where it will partially degrade into unwanted by-products.

Marcotullio (TU Delft; US 2012/0108829; corresponds with WO2012/057625) concerns producing furfural from pentoses and/or water soluble pentosans. The process comprises converting pentoses and/or water soluble pentosans in aqueous solution, in a first step, to furfural and, in a second step, feeding the aqueous solution containing furfural obtained in the first step to the top of a distillation column to produce an aqueous, liquid downflow, which column is heated at the bottom to produce an upflow water vapour flow, recovering a gaseous water and furfural containing product stream from the top of the column, compressing the vapour flow and condensing it on the hot side of a reboiler at the bottom of the column. However, in all trays below the inlet of the homogeneous catalyst, the evaporated furfural will again condense in a liquid phase with the catalyst and still form by-products. Thus, selectivity will be better in evaporators because the evaporated furfural is removed from the acid catalyst.

Thus, US 2012/0108829 discloses separation by distillation during reaction. This suffers from the disadvantage that the reaction continues as the mixture passes through the distillation column below the inlet of the liquid feed stream. This increases unwanted by-products.

In US 2012/0108829 / WO2012/057625 (TU Delft), an aqueous stream containing 2.03 wt% of pentoses is fed to an adiabatic pre-reactor and the resulting mixture containing 0.71 wt% of xylose and 0.87 wt% furfural is fed to a reactive distillation column. However, a reactive distillation column is not a film evaporator because, in each stage of the distillation column below the feeding line in the liquid phase, the catalyst is present. That means that the vapours, made in each stage below the feeding line, are condensed in the stage above the stage where they are vaporized. With the exception of the stages above the feeding line, the condensed vapours will come again in contact with the catalyst and therefore the catalyst can catalyse the reaction between the furfural made in the stage below and another furfural, or an intermediate or a side product or the sugars present in the liquid phase of that stage. Those reactions can lead to side products and decrease the selectivity and therefore the yield.

In contrast, in the method of the present invention, the vapours are removed from the liquid which contains the catalyst and, after condensing, they do not come back into contact again with the catalyst dissolved in the reactive liquid. This is an essential difference which increases the selectivity. So, in a reactive film evaporator, the catalyst is present in the liquid phase of the evaporator and catalyses the reactions, while the furfural which is evaporated at this evaporator escapes from that evaporator via the vapour phase and is condensed to a liquid which does not come in contact anymore with the catalyst.

This was even realized by the inventors of WO2012/057625 (TU Delft), as they admit in WO2015175840 on page 4 lines 1-3. There, the inventors said that “significant product loss will occur in the process of WO2012/057625 caused by undesirable reactions involving furfural, sugars and/or other reaction intermediates”. That happened because furfural which is made and vaporised in any stage below the feeding line will be condensed in a stage above the vaporizing stage and is again coming in contact with the catalyst and furfural, sugars and/or other reaction intermediates which can give side reactions.

In contrast, in the method of the present invention, in a reactive film evaporator, the vapours made are always coming from a liquid phase containing the catalyst in which, continuously, reagents (pentose sugars) are converted to product (furfural) and product (furfural) is removed via vaporisation and is then condensed to a liquid without coming in contact with the catalyst anymore after condensation.

WO2015/175840 (TU Delft) describes a kind of co-current bubble column in which the bubbles are the vapour/steam generated in the heat exchanger at the bottom where also the liquid inlet is. The reaction conditions in the bottom, as explained by the inventors, are such that, there, the pentose concentration is relatively high and furfural relatively low, so the furfural can do less undesirable reactions and, when the bubbles and liquid travel upwards through the column, the furfural concentration increases and sugar concentration decreases. In that way, according to the authors undesirable side reactions are minimised. See page 5, lines 15-22:

> “In the co-current flow the vapour stream still leaves the column from the top, but the liquid feed enters the column from the bottom. In this way the concentration of pentoses and/or pentosans will decrease from the bottom to the top of the column, opposite to the furfural concentration. The area of the column where losses may take place is thus limited somewhere in the middle of the column where both concentrations (of furfural and pentoses) are relatively low, so the risk of product loss due to formation of byproducts is minimized.”

This might improve the yield/selectivity compared to the reactive distillation in US 2012/0108829 / WO2012/057625 (TU Delft)

Instead of WO2015/175840’s co-current bubble column, the present invention aims to remove directly the furfural made as much as possible. Therefore we propose a film evaporator as reactor.

In our film evaporators, the energy is delivered by the hot surface in contact with the liquid containing catalysts and sugars. So the furfural made is evaporised at the surface and it has to travel only through a thin layer to escape from the reactive environment. Moreover, the vapours will be condensed in the next film evaporator to heat the surface and to evaporate newly fresh made furfural. Because it is only indirectly in contact, the condensed furfural does not come in contact any more with the catalyst and cannot be degraded.

In US 2,369,655 (Boehm), the reaction is not carried out in a film evaporator but in a kind of “guns” where the sugar containing juice is heated with live high temperature steam, and “the reactions are carried out with high rapidity” and “in such manner that the walls of the reaction chamber and passages therefrom are kept free from tarry and the like deposits by shooting the gun contents out of the gun chamber”. So at least the majority of the reaction takes place in such a gun chamber and NOT in an evaporator. This is supported by page 3 column 1of US 2,369,655 that the liquid entering the guns contains only traces of furfural (see below):

> “In addition traces of furfural and levulinic acid and propionic acid are identifiable in such liquor, and many other materials are doubtless present in small proportions.”

On page 4 of US 2,369,655, the authors disclose:

> “In the treatment in the gun 48 of liquor containing water solubles and made from gum wood chips for example, followed by explosion, **approximately two-thirds** of the water soluble solids are converted to volatile material. This volatile material comprises furfural and volatile organic acids, principally acetic and formic acids, together with other condensible and non-condensible materials.” (emphasis added)

Thus, US 2,369,655 discloses that the pentose sugars are converted up to high conversion in the gun.

In the gun, due to the relatively high pressure, most of it will be liquid. After the gun, the pressure is reduced and, there, volatiles are made due to the decrease in pressure (flashing), which happens in receiver 51. But this removal of furfural occurs AFTER the conversion happened and not, as is required in the method of the present invention, where the conversion is done on an evaporator and furfural is removed continuously as it is being formed.

WO 03/074781 (Chempolis) concerns a process for producing furfural, formic acid and acetic acid from spent pulp-cooking liquor. Chempolis works preferentially between 100 and 140°C, with high formic acid and acetic acid concentrations (~40%), long residence times - up to 10 hours - and end up with high solids (up to 95% at the end of the reaction). For example, they use low temperatures to avoid too much furfural production (which will be lost due to the high dilution of furfural in the vapours). Thus, Example 3 of WO 03/074781 uses formic and acetic acids to delignify the bagasse and they then react at 130 °C for 3 hours.

The present method takes a different approach to that of the prior art.

- Instead of concentrating the prehydrolysate before going to the reactive film evaporators, we use the diluted prehydrolysate as such.
- Instead of using high concentrations of organic acids, formic acid and acetic acid, we use a low concentration of an inorganic acid, sulfuric acid.
- Instead of using a relative low reaction temperature (130°C), we use a high temperature ~ at least 170ºC.
- Instead of evaporating almost all liquids and going to high, even very high, solids (95%), we evaporate part of the liquids and solids remain below 30% (w/w).
- Instead of going to complete conversion of the sugars, we go to partial conversion and recycle part of the remaining reaction solution to the prehydrolysate reactor.

In summary, in contrast, we go to high temperatures (at least 170ºC), low acid concentrations (mainly as inorganic acids (such as sulfuric acid)), short residence times (less than 10 minutes per evaporator) and not too high solids concentration - opposite to that in WO 03974781. Although we are opposite, compared to the prior art, we find, surprisingly, a lower steam consumption and better selectivity’s than the prior art.

The objectives of the method of the present invention are one or more of:

- evaporating furfural from the reaction medium comprising catalyst;
- preventing the evaporated furfural from further contacting the acid catalyst and,
- optionally, the energy requirements for this evaporation and removal step may be reduced by putting several evaporators in effect with each other.

Known processes for producing furfural from a pentose or pentosan-containing starting material share one or several of the shortcomings which include high capital costs, high energy requirement and problems of improving the yield of furfural, including reducing the amount of by-products.

Summary of the Invention

An effective method for producing furfural from a pentose or pentosan-containing starting material has been found.

According to the invention, there is provided a method for producing furfural from a pentose or pentosan-containing starting material, in a pressurised continuous flow reactor followed by one or more reaction vessels, wherein the one reaction vessel is an evaporator or wherein at least one of the more than one reaction vessels is an evaporator; and wherein the pentose or pentosan-containing starting material is brought as a liquid stream into the pressurised continuous flow reactor.

The method comprises bringing the liquid stream into a pressurised continuous flow reactor, wherein the mean temperature of the liquid stream in the pressurised continuous flow reactor is at least 170ºC;
bringing the liquid stream from the pressurised continuous flow reactor into one or more reaction vessels, wherein at least one of the one or more reaction vessels is a film evaporator; and, in each film evaporator,
providing a film of the liquid stream on heat exchangers of the evaporator, wherein the mean temperature of the liquid stream in the evaporator is at least 170ºC;
heating the film by indirectly contacting a heated vapour source with the film on the heat exchangers;
forming and simultaneously evaporating furfural, thereby separating a non-evaporated liquid fraction comprising an acid catalyst and unreacted pentose or pentosan-containing material from an evaporated fraction comprising evaporated furfural and preventing the separated evaporated furfural from further contacting the acid catalyst.

Optionally, the liquid stream comprises a prehydrolysate.

The liquid stream, optionally a prehydrolysate, that is brought into the pressurised continuous flow reactor has a solids contents of between 3 and 20% (w/w), optionally between 4 and 12% (w/w), and further optionally between 5 and 10% (w/).

The method reduces unwanted by-products by separating, immediately and continuously, an evaporated fraction comprising furfural from a liquid stream in an evaporator.

In an embodiment, the method reduces the energy requirements by indirectly heating a downstream evaporator with the evaporated fraction comprising evaporated furfural from an upstream evaporator. Optionally, a non-evaporated liquid fraction is separated from an evaporated fraction comprising furfural, in the evaporator.

Alternatively or optionally, the film evaporator is selected from the group consisting of rising film evaporators, falling film evaporators, wiped/agitated film evaporators and thin film evaporators and is optionally independently selected from the group consisting of rising film evaporators, falling film evaporators, and wiped/agitated film evaporators.

Alternatively or optionally, between 10 to 90% (w/w), optionally between 15 and 70% (w/w), further optionally between 20 and 50% (w/w), still further optionally between 20 and 30% (w/w), of the pentoses or pentosans in the liquid stream are converted to furfural and by-products in the pressurised continuous flow reactor; and / or wherein the residence time of the liquid stream in the pressurised continuous flow reactor is more than 5 seconds, optionally more than 10 seconds and / or less than 10 minutes; and / or

wherein the pressure in the pressurised continuous flow reactor system is in the range of from 0.1 to 1 MPa.

Alternatively or optionally, the acid catalyst is selected from the group consisting of hydrochloric acid, sulphuric acid, nitric acid, phosphoric acid (optionally from sulphuric acid, nitric acid, phosphoric acid)); and the acid catalyst may additionally comprise one or more organic acids such as, but not limited to, formic acid, acetic acid or levulinic acid. Still further optionally, the acid catalyst is selected from the group consisting of mixtures of one or more organic acids with one or more acid catalysts selected from hydrochloric acid, sulphuric acid, nitric acid, and phosphoric acid (optionally from sulphuric acid, nitric acid, phosphoric acid);

wherein, optionally, the acid catalyst is sulphuric acid; and / or

wherein the acid catalyst additionally comprises an organic acid selected from formic acid, acetic acid or levulinic acid, and mixtures thereof and / or

wherein the acid catalyst is a mixture of sulphuric acid and one or more organic acids selected from formic acid, acetic acid and levulinic acid.

The acid catalyst, selected from the group consisting of hydrochloric acid, sulphuric acid, nitric acid, and phosphoric acid, is present in an amount of 0.01% to 4% (w/w). While the acid catalyst may additionally comprise one or more organic acids, it is the acid catalyst, selected from the group consisting of hydrochloric acid, sulphuric acid, nitric acid, and phosphoric acid, that is present in an amount of 0.01% to 4% (w/w).

Alternatively or optionally, the method further comprises means for adding the acid catalyst to the pentose or pentosan-containing starting material upstream of the pressurised continuous flow reactor.

In an embodiment, the method is carried out in the pressurised continuous flow reactor in series with one reaction vessel that is an evaporator.

Alternatively or optionally, the liquid stream from the pressurised continuous flow reactor is brought to the evaporator and more than 50% (w/w), optionally more than 70%(w/w), further optionally more than 90%(w/w), of the pentoses or pentosans in the liquid stream to the pressurised continuous flow reactor are converted to furfural and by-products in the pressurised continuous flow reactor and in the evaporator.

Alternatively or optionally, the evaporator comprises a sump and a vapour collector and, in the evaporator, a non-evaporated liquid fraction is collected in the sump and an evaporated fraction comprising evaporated furfural is collected in the vapour collector; and the liquid stream for the evaporator optionally comprises at least some of the non-evaporated liquid fraction that has been recycled from the evaporator; and / or

wherein the evaporated fraction from the evaporator comprises at least 20% (w/w), optionally at least 30% (w/w), further optionally at least 40% (w/w), of the liquid stream to the pressurised continuous flow reactor.

Alternatively or optionally, the mean temperature of the liquid stream in the pressurised continuous flow reactor is at least 190ºC, optionally at least 210ºC, further optionally at least 230ºC; and / or

wherein the mean temperature of the liquid stream in the evaporator is at least 190ºC, optionally at least 210ºC, further optionally at least 230ºC.

In an embodiment, the method is carried out in a pressurised continuous flow reactor followed by a series of two or more reaction vessels, at least one of which is an evaporator; and wherein the pentose or pentosan-containing starting material is brought as a liquid stream into the pressurised continuous flow reactor.

Optionally, wherein the second most upstream reaction vessel in the series of reaction vessels is an evaporator; and / or the most downstream reaction vessel in the series of reaction vessels is not an evaporator; or

wherein, in the series of two or more reaction vessels, each reaction vessel in the series of reaction vessels is an evaporator; or

wherein the most downstream reaction vessel is a forced circulation evaporator and the other reaction vessels of the series of two or more reaction vessels, are selected from rising film evaporators and falling film evaporators; and are optionally falling film evaporators; or

wherein the at least one film evaporator is independently selected from the group consisting of a falling film evaporator or a series of falling film evaporators; a rising film evaporator or a series of rising film evaporators; a wiped/agitated film evaporator or a series of wiped/agitated film evaporators; a thin film evaporator or a series of thin film evaporators; or a mixture of rising film evaporators, falling film evaporators, wiped/agitated film evaporators, and thin film evaporators.

Further optionally, the mean temperature of the liquid stream in the pressurised continuous flow reactor is at least 190ºC, optionally at least 210ºC, further optionally at least 230ºC.

Still further optionally, in the at least one evaporator of the series of two or more reaction vessels, a non-evaporated liquid fraction is collected in a sump; and an evaporated fraction comprising evaporated furfural is collected in a vapour collector; and at least some of the liquid stream, in the at least one evaporator, comprises non-evaporated liquid fraction that has been recycled from the same evaporator; and / or

from a more upstream evaporator; and / or

from a more downstream evaporator, optionally the most downstream evaporator; and / or

wherein at least some of the liquid stream comprises recycled non-evaporated liquid fraction from the same evaporator in each of the one or more evaporators.

Still further optionally, the series of two or more reaction vessels are configured as multiple effect reaction vessels;

wherein, optionally, the, or each, evaporator comprises, in use,

> a heated vapour source for the upstream evaporator is for steam at a temperature that is higher than the mean temperature of the liquid stream in the upstream evaporator and wherein the heated vapour source for the one or more downstream evaporators is for vapour from the evaporated fraction comprising evaporated furfural, from an evaporator that is upstream of the one or more downstream evaporators;
>
> wherein the upstream evaporated fraction indirectly heats the liquid stream in the one or more downstream evaporators and condenses to produce a furfural condensate; and
>
> means for collecting the evaporated fraction comprising furfural condensate from the, or each, downstream evaporator.

Optionally, the residence time of the liquid stream in the, or each, evaporator, including the sump and the vapour collector, is less than 10 minutes, optionally less than 5 minutes, further optionally less than 1 minutes.

Optionally, the heated vapour source for the most upstream evaporator is for steam at a temperature that is at least 4°C higher, optionally at least 7°C higher, further optionally at least 10°C higher, than the mean temperature of the liquid stream in the most upstream evaporator.

In an embodiment, the series of two or more reaction vessels is an upstream evaporator, and a downstream evaporator; and wherein the upstream evaporator and the downstream evaporator are configured as multiple effect evaporators;

wherein, optionally, the liquid stream comprises at least some of the non-evaporated liquid fraction that has been recycled from the same evaporator; and / or at least some of the non-evaporated liquid fraction is transferred from the upstream evaporator into the downstream evaporator;

the method comprising

indirectly heating the liquid stream in the downstream evaporator with the upstream evaporated fraction comprising evaporated furfural, and condensing the upstream evaporated fraction comprising furfural to produce a furfural condensate; and

collecting the non-evaporated liquid fraction and the evaporated fraction comprising furfural from each evaporator.

Optionally, at least 10% (w/w), optionally at least 15% (w/w), further optionally at least 20% (w/w), of the liquid stream to each evaporator is evaporated from that evaporator; and / or

wherein more than 10% (w/w), more optionally more than 20% (w/w), more optionally more than 30% (w/w), still more optionally more than 40%(w/w), of the pentoses and pentosans in the liquid stream to each evaporator is converted in that evaporator; and / or

wherein the mean temperature of the liquid stream in each evaporator, independently falls by about 4 to 40ºC, optionally between about 4ºC to 20ºC, further optionally between about 4ºC to 10ºC, between the upstream evaporator and the downstream evaporator.

In an embodiment, the series of two or more reaction vessels is an upstream evaporator, and first and second downstream evaporators; and wherein the evaporators are configured as multiple effect evaporators;

wherein, optionally, the liquid stream comprises at least some of the non-evaporated liquid fraction that has been recycled from the same evaporator; and / or at least some of the non-evaporated liquid fraction from the upstream evaporator is for the first downstream evaporator and at least some of the non-evaporated liquid fraction from the first downstream evaporator is for the second downstream evaporator; and

wherein the heated vapour source for the upstream evaporator is for steam, the heated vapour source for the first downstream evaporator is for vapour from the evaporated fraction comprising evaporated furfural from the upstream evaporator and the heated vapour source for the second downstream evaporator is for vapour from the evaporated fraction comprising evaporated furfural from the first downstream evaporator; and / or wherein the upstream evaporator and the first downstream evaporator are falling film evaporators and the second downstream evaporator is a forced circulation evaporator.

In an embodiment, the series of two or more reaction vessels is an upstream evaporator, and first, second and third downstream evaporators; and wherein the evaporators are configured as multiple effect evaporators;

wherein, optionally, the liquid stream comprises at least some of the non-evaporated liquid fraction that has been recycled from the same evaporator; and / or at least some of the non-evaporated liquid fraction from the upstream evaporator is for the first downstream evaporator, at least some of the non-evaporated liquid fraction from the first downstream evaporator is for the second downstream evaporator, and at least some of the non-evaporated liquid fraction from the second downstream evaporator is for the third downstream evaporator; and / or

wherein the heated vapour source for the upstream evaporator is for steam, the heated vapour source for the first downstream evaporator is for the evaporated fraction comprising evaporated furfural from the upstream evaporator, the heated vapour source for the second downstream evaporator is for vapour from the evaporated fraction comprising evaporated furfural from the first downstream evaporator, and the heated vapour source for the third downstream evaporator is for vapour from the evaporated fraction comprising evaporated furfural from the second downstream evaporator; and / or

wherein the upstream evaporator and the first and second downstream evaporators are falling film evaporators and the third downstream evaporator is a forced circulation evaporator.

Optionally, the mean temperature of the liquid stream in the upstream evaporator and in the one or more downstream evaporators, independently falls by about 4 to 30ºC, optionally about 4 to 20ºC, further optionally about 4 to 15ºC, still further optionally between about 4ºC to 10ºC, between the upstream evaporator and each subsequent downstream evaporator.

In an embodiment, in the series of two or more reaction vessels, at least one of which is an evaporator, the series are not configured as multiple effect reaction vessels; and wherein the heated vapour source for each reaction vessel is, optionally, for steam; or

wherein the series of two or more reaction vessels is an evaporator, and wherein the evaporator is not configured as multiple effect evaporators; or

wherein the series of two or more reaction vessels is an upstream evaporator, and a downstream evaporator, and wherein the upstream evaporator and the downstream evaporator are not configured as multiple effect evaporators; or wherein the series of two or more of reaction vessels is an upstream evaporator, and first and second downstream evaporators; and wherein the evaporators are not configured as multiple effect evaporators; or

wherein the series of two or more reaction vessels is an upstream evaporator, and first, second and third downstream evaporators; and wherein the evaporators are not configured as multiple effect evaporators.

Optionally, the evaporated fraction is compressed and the compressed evaporated fraction indirectly heats the liquid stream in the same or another evaporator and then condenses to produce the furfural condensate.

Optionally, in relation to each of the embodiments, the evaporated fraction is subjected to mechanical vapour compression and the compressed evaporated fraction is used as a heat source for the same evaporator and/or another evaporator.

Brief Description of the Drawings

Figure 1 shows a flow reactor in series with 3 film evaporators all at the same temperature and heated with steam
Figure 2 shows a flow reactor in series with 2 film evaporators with heat integration via effect
Figure 3 shows a flow reactor in series with 3 film evaporators with heat integration via effect
Figure 4 shows a flow reactor in series with 4 film evaporators with heat integration via effect
Figure 5 shows a flow reactor in series with 1 film evaporator heated with steam

Detailed Description of the Invention

Definitions

The starting material is, preferably, a lignocellulosic biomass material that is rich in pentoses or pentosans. By a pentosan is understood a type of hemicellulose comprising a polymer or oligomer of pentoses. By a pentose is understood a monosaccharide with five carbon atoms. Examples of preferred pentoses include xylose and arabinose. Such pentoses can advantageously be converted into furfural.

By a lignocellulosic biomass material is herein understood a material containing lignocellulose obtained directly or indirectly from a biological source. Preferably it is understood to be a naturally obtained lignocellulosic material.

Examples of lignocellulosic biomass material include any lignocellulose containing biological materials, such as agriculture waste, forest residue, wood chips, straw, chaff, grain, grasses, corn, cornhusks, weeds, aquatic plants and/or hay; and/or any lignocellulose containing material of biological origin, such as some municipal waste or household waste.

Any lignocellulosic biomass material known to be suitable for hydrolysis by the person skilled in the art may be used in the method according to the present invention. The lignocellulosic biomass material typically includes hemicellulose, lignin and cellulose. The hemicellulose present in the lignocellulosic biomass material is processed to produce furfural.

The hemicellulose containing liquid stream may contain organic acids such as formic acid, acetic acid or levulinic acid. These acids can also ‘autohydrolyse’ the pentose sugars to furfural under suitable reaction conditions. The weak acidity of organic acids compared to sulfuric acid (for example) suggests that either higher temperatures, higher residence times and/or higher acid concentrations may be needed.

As used herein, the term “invention” or “present invention is a non-limiting term and is not intended to refer to any single variation of the particular invention but encompasses all possible variations described in the specification and recited in the claims.

As used herein, the term “about” modifying the quantity of an ingredient or reactant of the invention employed refers to variation in the numerical quantity that can occur, for example, through typical measuring and liquid handling procedures used for making concentrates or use solutions in the real world; through inadvertent error in these procedures; through differences in the manufacture, source, or purity of the ingredients employed to make the compositions or carry out the methods; and the like. The term “about” also encompasses amounts that differ due to different equilibrium conditions for a composition resulting from a particular initial mixture. Whether or not modified by the term “about’, the claims include equivalents to the quantities. The term “about” may mean within 10% of the reported numerical value, preferably within 5% of the reported numerical value.

As used herein, the term “pressurised continuous flow reactor system” means that the reaction mixture in the reactor system (liquid stream) is maintained in liquid phase at the reaction temperature due to pressurising by the vapour pressure of the liquid stream. The term “pressurised continuous flow reactor system” includes plug flow reactors. The pressure in the pressurised continuous flow reactor system may be in the range of from 0.1 to 10 MPa, preferably in the range of from 0.5 to 5 MPa. The pressurised continuous flow reactor system may comprise a single reaction vessel configured for and used in pressurised continuous flow operation, or a combination of serially connected reaction vessels configured for and used in pressurised continuous flow operation. The pressurised continuous flow reactor system may be selected from the group consisting of a continuous stirred tank reactor, a flow tube, a tubular reactor, a jet loop reactor, a cascade of continuous stirred tank reactors, and combinations thereof.

Conversion percentages, from the pentoses and pentosans in the pentose or pentosan-containing starting material, are calculated on a molar basis.

Evaporation percentages are calculated on a weight / weight basis.

The methods of the invention are carried out under autogenic pressure.

Film Evaporators

There are several types of evaporators available, each with their specific features, advantages, and disadvantages. Here is a brief summary of each type:

Rising Film Evaporator (RFE): In this type of evaporator, the vapour formed moves upwards and drags the liquid film, which continues to boil and generate more vapour. It gives excellent heat transfer performance and is generally inexpensive to manufacture. However, it has a higher pressure drop through the tubes compared to a falling-film evaporator and has a higher liquid hold-up.

Falling Film Evaporator (FFE): In this type of evaporator, the liquid stream is introduced at the upper end of the vertical tubes, and the film travels downwards by gravity, assisted by vapour drag. It has the inherent advantage of being a downflow device and produces thinner films and shorter residence times than a rising film evaporator. However, it is crucial, with falling film evaporators, to have a good distribution of the liquid stream uniformly to every tube and around the circumference of each tube.

Wiped / Agitated Thin Film Evaporators are equipped with wipers to distribute a thin liquid film uniformly across the heat transfer surface and have again shorter residence times than falling film evaporators.
Short-Tube Vertical Evaporator: It is still widely used in the industry, and circulation past the heating surface is induced by boiling in the tubes. The body is a vertical cylinder, usually of cast iron, and the tubes are expanded into horizontal tube sheets that span the body diameter. It has high heat-transfer coefficients at high temperature differences and is relatively inexpensive. However, it has poor heat transfer at low temperature differences and a high holdup that results in higher residence times and increased conversion to undesired by-products.

Horizontal-Tube Evaporator: In these types, hot medium is inside, and the mixture is outside of the tubes. It has a very low headroom and a large vapour-liquid disengaging area, but it is relatively expensive and has difficulties in maintaining proper liquid distribution and proper wetting of the surface.

Short Path Evaporators: These types of evaporators would be able to perform the task of evaporation, with proper residence time control, similar to FFE and RFE. However, the low furfural-concentrations in combination with the ease of evaporation makes these types of capital-intensive evaporators too expensive for this role.

Overall, the selection of the type of evaporator is mostly governed by the characteristics of the liquid stream and the product besides heat transfer considerations. Salting, scaling, fouling, product quality, corrosion, and foaming should also be considered.

Falling film evaporators (FFE) with recycle are suggested for use herein due to their good heat transfer coefficients and ability to maintain adequate residence time.

Evaporators are usually 1, 3 or 6 m in length. If a longer residence time is desired, either a longer evaporator is chosen and / or the liquid stream from an evaporator may be recycled back into the same evaporator.

Where 1 evaporator is employed, more than 50%, optionally more than 70%, further optionally more than 90%, of the pentoses or pentosans in the liquid stream are converted to furfural and by-products in the evaporator.

Where 2 evaporators are employed in series, more than 10%, more optionally more than 20%, more optionally more than 30%, still more optionally more than 40%, of the pentoses and pentosans in the liquid stream to each evaporator are converted in each evaporator.

Where 3 or 4 evaporators are employed in series, more than 10%, more optionally more than 20%, more optionally more than 30%, still more optionally more than 40%, of the pentoses and pentosans in the liquid stream to each evaporator are converted in each evaporator.

The % conversion in each reaction vessel may be modified by maintaining the higher reaction temperature; using a higher acid concentration; using a longer residence time by either making the tubes longer (not practical) or by recycling to the same evaporator; and / or by including more tubes in each evaporator.

Where a single evaporator is employed, at least 20%, optionally at least 25%, further optionally at least 30%, of the liquid stream is evaporated from the evaporator.

Where 2 evaporators are employed in series, at least 15%- 40%, optionally at least 20%, further optionally at least 25%, still further optionally at least 30%, of the liquid stream is evaporated from the upstream evaporator.

In the subsequent liquid streams, the volume is progressively reduced and it’s the energy efficiency of the heat transfer from the furfural-containing vapour that determines the evaporation rate in each subsequent downstream evaporator.

Where 3 or 4 evaporators are employed in series, at least 15% and optionally no more than 35% of the liquid stream is evaporated from the upstream evaporator.

The methods described herein are illustrated in the following examples. From the above discussion and these examples, one skilled in the art can ascertain the essential characteristics of this invention, and without departing from the spirit and scope thereof, can make various changes and modifications of the invention to adapt it to various uses and conditions. The methods in these examples have been carried out under autogenic pressure.

Example 1: 3 film evaporators in series all at the same temperature heated with steam

Referring to Figure 1, a synthetic aqueous prehydrolysate (11) containing xylose is optionally preheated and is mixed with acid catalyst (optionally sulfuric acid) up to the appropriate acid concentration and brought in a pressurised continuous flow reactor via 10 to convert part of the xylose until, at the exit of the reactor, a molar ratio of furfural/not-converted xylose of at least 0.15 is obtained. Subsequently, the product mixture is brought into the film evaporator 1. The film evaporator 1 is heated via indirect heat exchange with steam (15) up to a temperature above 170°C. The condensate of the steam leaves the film evaporator 1 via pipe 16. The total residence time, including optional partial recycle, over the first film evaporator 1 was sufficient to reach a desired conversion. During the conversion, part of the water and furfural is evaporated (between 15% and 35% of the total liquid stream entering the first film evaporator 1) and the vapors are enriched in furfural compared to the liquid phase. These vapors leave the first film evaporator 1 via pipe (13).

The concentrated hydrolysate containing water, furfural and xylose together with some intermediates, side products, heavies and sulfuric acid leaves the film evaporator via pipe (12) and is called concentrate 1.

Concentrate 1 enters the second film evaporator 2 at a similar temperature as in the first film evaporator 1 and is heated via indirect heat exchange with steam (25) at a temperature similar to that of the first film evaporator 1. The condensate of the steam leaves the second film evaporator 2 via pipe (26). The total residence time, including optional partial recycle, over the second film evaporator 2 was sufficient to reach a desired conversion of the xylose. During the conversion, part of the water and furfural is evaporated (for example, between 15% and 35% of the total liquid stream entering the second film evaporator 2) and the vapors are enriched in furfural compared to the liquid phase. These vapors leave the second film evaporator 2 via pipe (23).

The concentrated hydrolysate containing water, furfural and xylose together with some intermediates, side products, heavies and sulfuric acid leaves the second film evaporator 2 via pipe (22) and is called concentrate 2.

Concentrate 2 enters the third film evaporator 3 at a similar temperature to that of the second film evaporator 2 and is heated via indirect heat exchange with steam (35) at a temperature similar to that of the second film evaporator 2. The condensate of the steam leaves the third film evaporator 3 via pipe (36). The total residence time, including optional partial recycle, over the third film evaporator 3 was sufficient to reach a desired conversion of the xylose. During the conversion, part of the water and furfural is evaporated (for example, between 15% and 35% of the total liquid stream entering the third form evaporator 3) and the vapors are enriched in furfural compared to the liquid phase. These vapors leave the third film evaporator 3 via pipe (33).

The concentrated hydrolysate containing water, furfural and xylose together with some intermediates, side products, heavies and sulfuric acid leaves the third film evaporator 3 via pipe (32) and is called concentrate 3.

The vapors containing furfural optionally can be combined and condensed with (50) cooling water or with another stream which can be heated or can be used for heating a distillation column or the heat can be integrated in another manner, optionally via (47) to pre-heat the prehydrolysate. The condensed furfural can be further separated and purified in a conventional furfural distillation and purification.

Concentrate 3 can be recycled to the first film evaporator 1. In that case, a purge is needed to avoid blowing up the reaction section with heavies, optionally salts. The concentrate 3 can also be recycled to the pretreatment. It can be neutralized and the furfural can be recovered and it can also be sent to the waste water treatment. In all 3 previous cases, at least part of the furfural will be recovered in addition, but in most cases it will require extra energy.

Example 2: 2 film evaporators in series with heat integration via effect

Referring to Figure 2, a synthetic aqueous prehydrolysate containing xylose, is optionally preheated and is mixed with acid catalyst (optionally sulfuric acid) up to the appropriate acid concentration and brought in a pressurised continuous flow reactor via 10 to convert part of the xylose until, at the exit of the reactor, a molar ratio of furfural/not-converted xylose of at least 0.15 is obtained. Subsequently, the product mixture is brought into the first film evaporator 1 via 11. The first film evaporator 1 is heated via indirect heat exchange with steam (15) up to a temperature above 170°C. The condensate of the steam leaves the first film evaporator 1 via pipe 16. The total residence time including optionally partial recycle over the first film evaporator 1 was sufficient to reach a desired conversion of the xylose. During the conversion, part of the water and furfural is evaporated (at least 10%; most optionally at least 40% of the total liquid stream entering the first film evaporator 1) and the vapors are enriched in furfural compared to the liquid phase. These vapors leave the film evaporator via pipe (13).

More than 10%, more optionally more than 20%, more optionally more than 30%, still more optionally more than 40%, of the pentoses and pentosans in the liquid stream to each evaporator are converted in each evaporator.

The concentrated hydrolysate containing water, furfural and xylose together with some intermediates, side products, heavies and sulfuric acid leaves the film evaporator via pipe (12) and is called concentrate 1.

Concentrate 1 can be optionally flashed in a flash vessel to the temperature which is between 4 and 40°C below the temperature of the first film evaporator 1 and, after that, enters film evaporator 2 via pipe (12). The second film evaporator 2 operates at a temperature between 4 and 40°C below the temperature of first film evaporator 1 and is indirectly heated with the furfural containing vapors (13) of first film evaporator 1. The condensate of those furfural containing vapors leaves the second film evaporator 2 via pipe (17). The residence time, including optional recycle, is at a temperature, and higher acid concentration that is sufficient to reach a desired conversion of the remaining xylose. In the second film evaporator 2, part of the water and furfural is evaporated and furfural is enriched in the vapor stream. The furfural vapors, produced in the second film evaporator 2, leave the film evaporator via pipe (23).

The vapors containing furfural can be condensed with (50) cooling water or with another stream which can be heated or can be used for heating a distillation column or the heat can be integrated in another manner, for example, to heat the prehydrolysate with or optionally without combining the streams. The condensed furfural can be further separated and purified in a conventional furfural distillation and purification.

The concentrated hydrolysate 2 containing water, furfural and remaining xylose together with some intermediates, side products, heavies and sulfuric acid leaves the film evaporator via pipe (22) and is called concentrate 2. This concentrate can be recycled to the first film evaporator 1. In that case, a purge is needed to avoid blowing up the reaction section with heavies, optionally salts. The concentrate 2 can also be recycled to the pretreatment. It can be neutralized and the furfural can be recovered and it can also be sent to the waste water treatment. In the latter 3 cases, at least part of the furfural will be recovered in addition, but in most cases it will require extra energy.

Example 3: 3 film evaporators in series with heat integration via effect

Referring to Figure 3, a synthetic aqueous prehydrolysate (11) containing xylose is optionally preheated and is mixed with acid catalyst (optionally sulfuric acid) up to the appropriate acid concentration and brought in a pressurised continuous flow reactor via 10 to convert part of the xylose until, at the exit of the reactor, a molar ratio of furfural/not-converted xylose of at least 0.15 is obtained. Subsequently, the product mixture is brought into the film evaporator 1. The film evaporator 1 is heated via indirect heat exchange with steam (15) up to a temperature above 170°C.

The condensate of the steam leaves the film evaporator via pipe 16. The total residence time, including optional partial recycle over the film evaporator, was sufficient to reach a desired conversion of the xylose. During the conversion, part of the water and furfural is evaporated (for example, between 15% and 35% of the total liquid stream entering the first evaporator 1) and the vapors are enriched in furfural compared to the liquid phase. These vapors leave the film evaporator via pipe (13).

The concentrated hydrolysate containing water, furfural and xylose together with some intermediates, side products, heavies and sulfuric acid leaves the film evaporator via pipe (12) and is called concentrate 1.

Concentrate 1 is at a high temperature and can be optionally flashed in a flash vessel to the temperature of the second film evaporator 2 which is between 4 and 40°C below the temperature of the first film evaporator 1 and, after that, enters the second film evaporator 2. The second film evaporator 2 operates at a temperature between 4 and 40°C below the temperature of first film evaporator 1 and is indirectly heated with the furfural containing vapors (13) of first film evaporator 1. The condensate of those furfural containing vapors leaves the second film evaporator 2 via pipe (17). The residence time, including optional recycle, is at a temperature, and higher acid concentration that are sufficient to reach a desired conversion of the remaining xylose. In the second film evaporator 2, again part of the water and furfural is evaporated and furfural is enriched in the vapor stream. The furfural vapors leave the film evaporator via pipe 23.

The concentrated hydrolysate containing water, furfural and xylose together with some intermediates, side products, heavies and sulfuric acid leaves the second film evaporator 2 via pipe (22) and is called concentrate 2.

Concentrate 2 can be optionally flashed in a flash vessel to the temperature of a third film evaporator 3, which is between 4 and 40°C below the temperature of the second film evaporator 2 and, after that, enters the third film evaporator 3 via pipe (22). The third film evaporator 3 operates at a temperature between 4 and 40°C below the temperature of the second film evaporator 2 and is indirectly heated with the furfural containing vapors (23) of second film evaporator 2. The condensate of those furfural containing vapors leaves the third film evaporator 3 via pipe (27). The residence time, including optional recycle, is at a temperature, and higher acid concentration that are sufficient to reach a desired conversion of the remaining xylose. In the third film evaporator 3, again part of the water and furfural is evaporated and furfural is enriched in the vapor stream. The furfural vapors leave the film evaporator via pipe (33).

The concentrated hydrolysate containing water, furfural and xylose together with some intermediates, side products, heavies and sulfuric acid leaves the third film evaporator 3 via pipe (32) and is called concentrate 3.

The vapors containing furfural can be condensed with (50) cooling water or with another stream which can be heated or can be used for heating a distillation column or the heat can be integrated in another manner, for example, to heat the prehydrolysate with, or optionally without, combining the streams. The condensed furfural can be further separated and purified in a conventional furfural distillation and purification.

The concentrated hydrolysate 3 containing water, furfural and remaining xylose together with some intermediates, side products, heavies and sulfuric acid leaves the film evaporator via pipe (32) and is called concentrate 3. This concentrate 3 can be recycled to the first film evaporator 1. In that case, a purge is needed to avoid blowing up the reaction section with heavies, optionally salts. The concentrate can also be recycled to the pretreatment. It can be neutralized and the furfural can be recovered and it can also be sent to the waste water treatment. In the latter 3 cases, at least part of the furfural will be recovered in addition, but in most cases it will require extra energy.

Example 4: 4 film evaporators in series with heat integration via effect

Referring to Figure 4, a synthetic aqueous prehydrolysate (11) containing xylose is optionally preheated and is mixed with acid catalyst (optionally sulfuric acid) up to the appropriate acid concentration and brought in a pressurised continuous flow reactor via 10 to convert part of the xylose until, at the exit of the reactor, a molar ratio of furfural/not-converted xylose of at least 0.15 is obtained. Subsequently, the product mixture is brought into the film evaporator 1. The film evaporator 1 is heated via indirect heat exchange with steam (15) up to a temperature above 170°C. The condensate of the steam leaves the film evaporator via pipe 16. The total residence time including optional partial recycle over the film evaporator 1 was sufficient to reach a desired conversion of the xylose. During the conversion, part of the water and furfural is evaporated (for example, between 10% and 25% of the total liquid stream entering the first evaporator 1) and the vapors are enriched in furfural compared to the liquid phase. These vapors leave the film evaporator via pipe (13).

The concentrated hydrolysate containing water, furfural and xylose together with some intermediates, side products, heavies and sulfuric acid leaves the first film evaporator 1 via pipe (12) and is called concentrate 1.

Concentrate 1 is at a high temperature and can be optionally flashed in a flash vessel to the temperature of the second film evaporator which is between 4 and 40°C below the temperature of the first film evaporator 1 and, after that, enters the second film evaporator 2. The second film evaporator 2 operates at a temperature between 4 and 40°C below the temperature of the first film evaporator 1 and is indirectly heated with the furfural containing vapors (13) of the first film evaporator 1. The condensate of those furfural containing vapors leaves the second film evaporator 2 via pipe (17). The residence time, including optional recycle, is at a temperature, and higher acid concentration that are sufficient to reach a desired conversion of the remaining xylose In the second film evaporator 2, again part of the water and furfural is evaporated and furfural is enriched in the vapor stream. The furfural vapors leave the film evaporator via pipe 23.

The concentrated hydrolysate containing water, furfural and xylose together with some intermediates, side products, heavies and sulfuric acid leaves the second film evaporator 2 via pipe (22) and is called concentrate 2.

Concentrate 2 can be optionally flashed in a flash vessel to the temperature of the third film evaporator 3 which is between 4 and 40°C below the temperature of the second film evaporator 2 and, after that, enters the third film evaporator 3 via pipe (22). The third film evaporator 3 operates at a temperature between 4 and 40°C below the temperature of the second film evaporator 2 and is indirectly heated with the furfural containing vapors (23) of the second film evaporator 2. The condensate of those furfural containing vapors leaves the third film evaporator 3 via pipe (27). The residence time, including optional recycle, is at a temperature, and higher acid concentration that are sufficient to reach a desired conversion of the remaining xylose. In the third film evaporator 3, again part of the water and furfural is evaporated and furfural is enriched in the vapor stream. The furfural vapors leave the third film evaporator 3 via pipe (33).

The concentrated hydrolysate containing water, furfural and xylose together with some intermediates, side products, heavies and sulfuric acid leaves the third film evaporator 3 via pipe (32) and is called concentrate 3.

Concentrate 3 can be optionally flashed in a flash vessel to the temperature of the fourth film evaporator 4 which is between 4 and 40°C below the temperature of the third film evaporator 3 and, after that, enters the fourth film evaporator 4 via pipe (32). The fourth film evaporator 4 operates at a temperature between 4 and 40°C below the temperature of the third film evaporator 3 and is indirectly heated with the furfural containing vapors (33) of the third film evaporator 3. The condensate of those furfural containing vapors leaves the fourth film evaporator 4 via pipe (37). The residence time, including optional recycle, is at a temperature, and higher acid concentration that are sufficient to reach a desired conversion of the remaining xylose. In the fourth film evaporator 4, again part of the water and furfural is evaporated and furfural is enriched in the vapor stream. The furfural vapors leave the film evaporator via pipe (43).

The concentrated hydrolysate containing water, furfural and xylose together with some intermediates, side products, heavies and sulfuric acid leaves the fourth film evaporator 4 via pipe (42) and is called concentrate 4.

The vapors containing furfural can be condensed with (50) cooling water or with another stream which can be heated or can be used for heating a distillation column or the heat can be integrated in another manner, for example, to heat the prehydrolysate with or optionally without combining the streams. The condensed furfural can be further separated and purified in a conventional furfural distillation and purification.

The concentrated hydrolysate 4 containing water, furfural and remaining xylose together with some intermediates, side products, heavies and sulfuric acid leaves the fourth film evaporator 4 via pipe (42) and is called concentrate 4. This concentrate 4 can be recycled to the first film evaporator 1. In that case, a purge is needed to avoid blowing up the reaction section with heavies, optionally salts. The concentrate 4 can also be recycled to the pretreatment. It can be neutralized and the furfural can be recovered and it can also be sent to the waste water treatment. In the latter 3 cases, at least part of the furfural will be recovered in addition, but in most cases it will require extra energy.

Example 5: one film evaporator

Referring to Figure 5, a synthetic aqueous prehydrolysate containing xylose, is optionally preheated and is mixed with acid catalyst (optionally sulfuric acid) up to the appropriate acid concentration and brought in a pressurised continuous flow reactor via 10 to convert part of the xylose until, at the exit of the reactor, a molar ratio of furfural/not-converted xylose of at least 0.15 is obtained. Subsequently, the product mixture is brought into the film evaporator 1 via 11. The film evaporator 1 is heated via indirect heat exchange with steam (15) up to a temperature above 170°C. The condensate of the steam leaves the film evaporator 1 via pipe 16. The total residence time including optionally partial recycle over the film evaporator 1 (not shown) was sufficient to reach a desired conversion of the xylose. During the conversion, part of the water and furfural is evaporated (for example, between 20% and 50% of the total liquid stream entering the film evaporator 1) and the vapors are enriched in furfural compared to the liquid phase. These vapors leave the film evaporator via pipe (13).

The concentrated hydrolysate containing water, furfural and xylose together with some intermediates, side products, heavies and sulfuric acid leaves the film evaporator 1 via pipe (12) and is called concentrate 1.

Concentrate 1 may recycle to the film evaporator 1 in order to increase the total residence time in film evaporator 1. Alternatively, the overall length of the film evaporator 1 may be increased, again to increase the total residence time in film evaporator 1.

The invention is not limited to the embodiments described herein but can be amended or modified without departing from the scope of the present invention.

Claims:

1. A method for producing furfural from a liquid stream of a pentose or pentosan-containing starting material, the method comprising:

bringing the liquid stream into a pressurised continuous flow reactor, wherein the mean temperature of the liquid stream in the pressurised continuous flow reactor is at least 170ºC;

bringing the liquid stream from the pressurised continuous flow reactor into one or more reaction vessels, wherein at least one of the one or more reaction vessels is a film evaporator; and, in each film evaporator,

providing a film of the liquid stream on heat exchangers of the evaporator, wherein the mean temperature of the liquid stream in the evaporator is at least 170ºC;

heating the film by indirectly contacting a heated vapour source with the film on the heat exchangers;

forming and simultaneously evaporating furfural, thereby separating a non-evaporated liquid fraction comprising an acid catalyst and unreacted pentose or pentosan-containing material from an evaporated fraction comprising evaporated furfural and preventing the separated evaporated furfural from further contacting the acid catalyst.

2. The method of Claim 1, wherein the film evaporator is selected from the group consisting of rising film evaporators, falling film evaporators, wiped/agitated film evaporators and thin film evaporators and is optionally independently selected from the group consisting of rising film evaporators, falling film evaporators, and wiped/agitated film evaporators.

3. The method of Claim 1 or 2, wherein between 10 to 90% (w/w), optionally between 15 and 70% (w/w), further optionally between 20 and 50% (w/w), still further optionally between 20 and 30% (w/w), of the pentoses or pentosans in the liquid stream are converted to furfural and by-products in the pressurised continuous flow reactor; and / or

wherein the residence time of the liquid stream in the pressurised continuous flow reactor is more than 5 seconds, optionally more than 10 seconds and / or less than 10 minutes.

4. The method of any one of Claims 1 to 3, wherein the mean pressure in the pressurised continuous flow reactor is in the range of from 0.1 to 1 MPa.

5. The method of any one of Claims 1 to 4, wherein the acid catalyst is selected from the group consisting of hydrochloric acid, sulphuric acid, nitric acid, phosphoric acid;optionally the acid catalyst additionally comprises one or more organic acids optionally selected from the group consisting of formic acid, acetic acid and levulinic acid, further optionally, the acid catalyst comprises mixtures of one or more organic acids with one or more acid catalysts selected from hydrochloric acid, sulphuric acid, nitric acid, and phosphoric acid;

wherein, optionally, the acid catalyst is sulphuric acid; and / or

wherein the acid catalyst additionally comprises an organic acid selected from formic acid, acetic acid or levulinic acid, and mixtures thereof and / or

wherein the acid catalyst is a mixture of sulphuric acid and one or more organic acids selected from formic acid, acetic acid and levulinic acid.

6. The method of Claim 5, further comprising means for adding the acid catalyst to the pentose or pentosan-containing starting material upstream of the pressurised continuous flow reactor.

7. The method of any one of Claims 1 to 6, wherein the method is carried out in the pressurised continuous flow reactor in series with one reaction vessel that is a film evaporator.

8. The method of any one of Claims 1 to 7, wherein more than 50% (w/w), optionally more than 70% (w/w), further optionally more than 90% (w/w), of the pentoses or pentosans in the liquid stream to the pressurised continuous flow reactor are converted to furfural and by-products in the pressurised continuous flow reactor and in the one or more reaction vessels.

9. The method of any one of Claims 1 to 8, wherein the evaporator comprises a sump and a vapour collector and, in the evaporator, a non-evaporated liquid fraction is collected in the sump and an evaporated fraction comprising evaporated furfural is collected in the vapour collector; and the liquid stream for the evaporator optionally comprises at least some of the non-evaporated liquid fraction that has been recycled from the evaporator; and / or

wherein the evaporated fraction from the evaporator of the one or more reaction vessels comprises at least 20% (w/w), optionally at least 30% (w/w), further optionally at least 40% (w/w), of the liquid stream to the pressurised continuous flow reactor.

10. The method of any one of Claims 1 to 9, wherein the mean temperature of the liquid stream in the pressurised continuous flow reactor is at least 190ºC, optionally at least 210ºC, further optionally at least 230ºC; and / or

wherein the mean temperature of the liquid stream in the evaporator is at least 190ºC, optionally at least 210ºC, further optionally at least 230ºC.

11. The method of any one of Claims 1 to 6, wherein the method is carried out in a pressurised continuous flow reactor followed by a series of two or more reaction vessels, at least one of which is a film evaporator.

12. The method of Claim 11, wherein the second most upstream reaction vessel in the series of reaction vessels is a film evaporator; and / or the most downstream reaction vessel in the series of reaction vessels is not an evaporator; or

wherein, in the series of two or more reaction vessels, each reaction vessel in the series of reaction vessels is a film evaporator; or

wherein the most downstream reaction vessel is a forced circulation evaporator and the other reaction vessels of the series of two or more reaction vessels, are selected from rising film evaporators, falling film evaporators, and thin film evaporators; and are optionally falling film evaporators; or

wherein the at least one evaporator is independently selected from the group consisting of a falling film evaporator or a series of falling film evaporators; a rising film evaporator or a series of rising film evaporators; a wiped/agitated film evaporator or a series of wiped/agitated film evaporators; a thin film evaporator or a series of thin film evaporators; or a mixture of rising film evaporators, falling film evaporators, wiped/agitated film evaporators, and thin film evaporators.

13. The method of Claim 11 or 12, wherein the mean temperature of the liquid stream in the pressurised continuous flow reactor is at least 190ºC, optionally at least 210ºC, further optionally at least 230ºC.

14. The method of any one of Claims 11 to 13, wherein, in the at least one evaporator of the series of two or more reaction vessels, a non-evaporated liquid fraction is collected in a sump; and an evaporated fraction comprising evaporated furfural is collected in a vapour collector; and at least some of the liquid stream, in the at least one evaporator, comprises non-evaporated liquid fraction that has been recycled from the same evaporator; and / or

from a more upstream evaporator; and / or

from a more downstream evaporator, optionally the most downstream evaporator; and / or

wherein at least some of the liquid stream comprises recycled non-evaporated liquid fraction from the same evaporator in each of the one or more evaporators.

15. The method of any one of Claims 11 to 14, wherein the series of two or more reaction vessels are configured as multiple effect reaction vessels;

wherein, optionally, the, or each, evaporator comprises, in use, the heated vapour source for the upstream evaporator is for steam at a temperature that is higher than the mean temperature of the liquid stream in the upstream evaporator and wherein the heated vapour source for the one or more downstream evaporators is for vapour from the evaporated fraction comprising evaporated furfural, from an evaporator that is upstream of the one or more downstream evaporators;

wherein the upstream evaporated fraction indirectly heats the liquid stream in the one or more downstream evaporators and condenses to produce a furfural condensate; and

means for collecting the evaporated fraction comprising furfural condensate from the, or each, downstream evaporator.

16. The method of any one of Claims 11 to 15, wherein the residence time of the liquid stream in the, or each, evaporator, including the sump and the vapour collector, is less than 10 minutes, optionally less than 5 minutes, further optionally less than 1 minutes.

17. The method of Claim 15 or 16, wherein the heated vapour source for the most upstream evaporator is for steam at a temperature that is at least 4ºC higher, optionally at least 7ºC higher, further optionally at least 10ºC higher, than the mean temperature of the liquid stream in the most upstream evaporator.

18. The method of any one of Claims 1 to 17, wherein the series of two or more reaction vessels is an upstream evaporator, and a downstream evaporator; and wherein the upstream evaporator and the downstream evaporator are configured as multiple effect evaporators;

wherein, optionally, the liquid stream comprises at least some of the non-evaporated liquid fraction that has been recycled from the same evaporator; and / or at least some of the non-evaporated liquid fraction is transferred from the upstream evaporator into the downstream evaporator;

the method comprising

indirectly heating the liquid stream in the downstream evaporator with the upstream evaporated fraction comprising evaporated furfural, and condensing the upstream evaporated fraction comprising furfural to produce a furfural condensate; and

collecting the non-evaporated liquid fraction and the evaporated fraction comprising furfural from each evaporator.

19. The method of Claim 18, wherein at least 10% (w/w), optionally at least 15% (w/w), further optionally at least 20% (w/w), of the liquid stream to each evaporator is evaporated from that evaporator; and / or

wherein more than 10% (w/w), more optionally more than 20% (w/w), more optionally more than 30% (w/w), still more optionally more than 40% (w/w), of the pentoses and pentosans in the liquid stream to each evaporator is converted in that evaporator; and / or

wherein the mean temperature of the liquid stream in each evaporator, independently falls by about 4 to 40ºC, optionally between about 4ºC to 20ºC, further optionally between about 4ºC to 10ºC, between the upstream evaporator and the downstream evaporator.

20. The method of any one of Claims 1 to 17, wherein the series of two or more reaction vessels is an upstream evaporator, and first and second downstream evaporators; and wherein the evaporators are configured as multiple effect evaporators;

wherein, optionally, the liquid stream comprises at least some of the non-evaporated liquid fraction that has been recycled from the same evaporator; and / or at least some of the non-evaporated liquid fraction from the upstream evaporator is for the first downstream evaporator and at least some of the non-evaporated liquid fraction from the first downstream evaporator is for the second downstream evaporator; and

wherein the heated vapour source for the upstream evaporator is for steam, the heated vapour source for the first downstream evaporator is for vapour from the evaporated fraction comprising evaporated furfural from the upstream evaporator and the heated vapour source for the second downstream evaporator is for vapour from the evaporated fraction comprising evaporated furfural from the first downstream evaporator; and / or

wherein the upstream evaporator and the first downstream evaporator are falling film evaporators and the second downstream evaporator is a forced circulation evaporator.

21. The method of any one of Claims 1 to 17, wherein the series of two or more reaction vessels is an upstream evaporator, and first, second and third downstream evaporators; and wherein the evaporators are configured as multiple effect evaporators;

wherein, optionally, the liquid stream comprises at least some of the non-evaporated liquid fraction that has been recycled from the same evaporator; and / or at least some of the non-evaporated liquid fraction from the upstream evaporator is for the first downstream evaporator, at least some of the non-evaporated liquid fraction from the first downstream evaporator is for the second downstream evaporator, and at least some of the non-evaporated liquid fraction from the second downstream evaporator is for the third downstream evaporator; and / or

wherein the heated vapour source for the upstream evaporator is for steam, the heated vapour source for the first downstream evaporator is for the evaporated fraction comprising evaporated furfural from the upstream evaporator, the heated vapour source for the second downstream evaporator is for vapour from the evaporated fraction comprising evaporated furfural from the first downstream evaporator, and the heated vapour source for the third downstream evaporator is for vapour from the evaporated fraction comprising evaporated furfural from the second downstream evaporator; and / or

wherein the upstream evaporator and the first and second downstream evaporators are falling film evaporators and the third downstream evaporator is a forced circulation evaporator.

22. The method of any one of Claims 15 to 21, wherein the mean temperature of the liquid stream in the upstream evaporator and in the one or more downstream evaporators, independently falls by about 4 to 30ºC, optionally about 4 to 20ºC, further optionally about 4 to 15ºC, still further optionally between about 4ºC to 10ºC, between the upstream evaporator and each subsequent downstream evaporator.

23. The method of any one of Claims 1 to 16, wherein, in the series of two or more reaction vessels, at least one of which is an evaporator, the series are not configured as multiple effect reaction vessels; and wherein the heated vapour source for each reaction vessel is, optionally, for steam; or

wherein the series of two or more reaction vessels is an evaporator, and wherein the evaporator is not configured as multiple effect evaporators; or

wherein the series of two or more reaction vessels is an upstream evaporator, and a downstream evaporator, and wherein the upstream evaporator and the downstream evaporator are not configured as multiple effect evaporators; or

wherein the series of two or more of reaction vessels is an upstream evaporator, and first and second downstream evaporators; and wherein the evaporators are not configured as multiple effect evaporators; or

wherein the series of two or more reaction vessels is an upstream evaporator, and first, second and third downstream evaporators; and wherein the evaporators are not configured as multiple effect evaporators.

24. The method of any one of Claims 1 to 23, wherein the evaporated fraction is compressed and the compressed evaporated fraction indirectly heats the liquid stream in the same or another evaporator and then condenses to produce the furfural condensate.

Figure 1

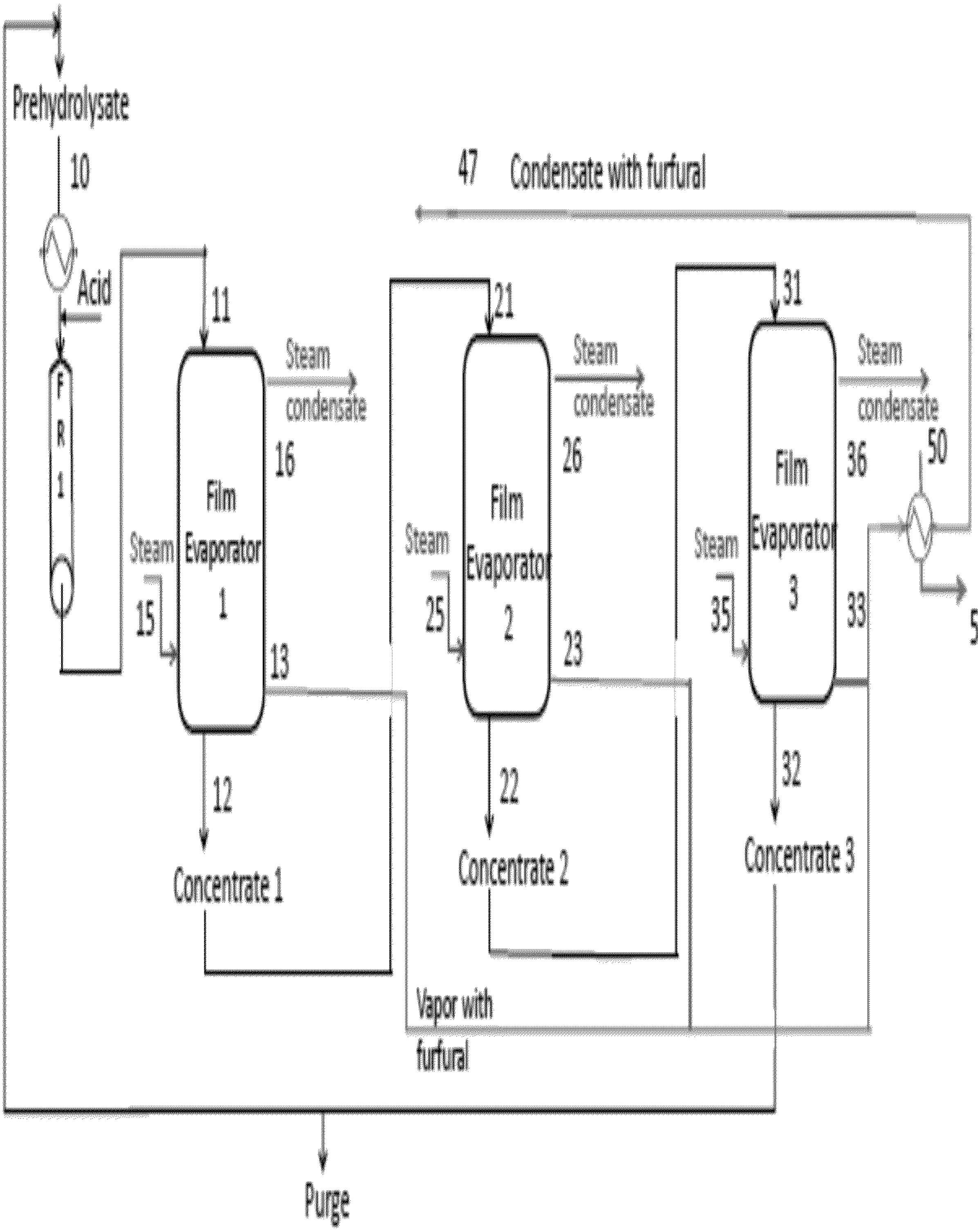

Prehydrolysate
10
Acid
F R 1
11
Film Evaporator 1
Steam condensate
16
Steam
15
13
12
Concentrate 1
47
Condensate with furfural
21
Film Evaporator 2
Steam condensate
26
Steam
25
23
22
Concentrate 2
31
Film Evaporator 3
Steam condensate
36
50
Steam
35
33
51
32
Concentrate 3
Vapor with furfural
Purge

Figure 2

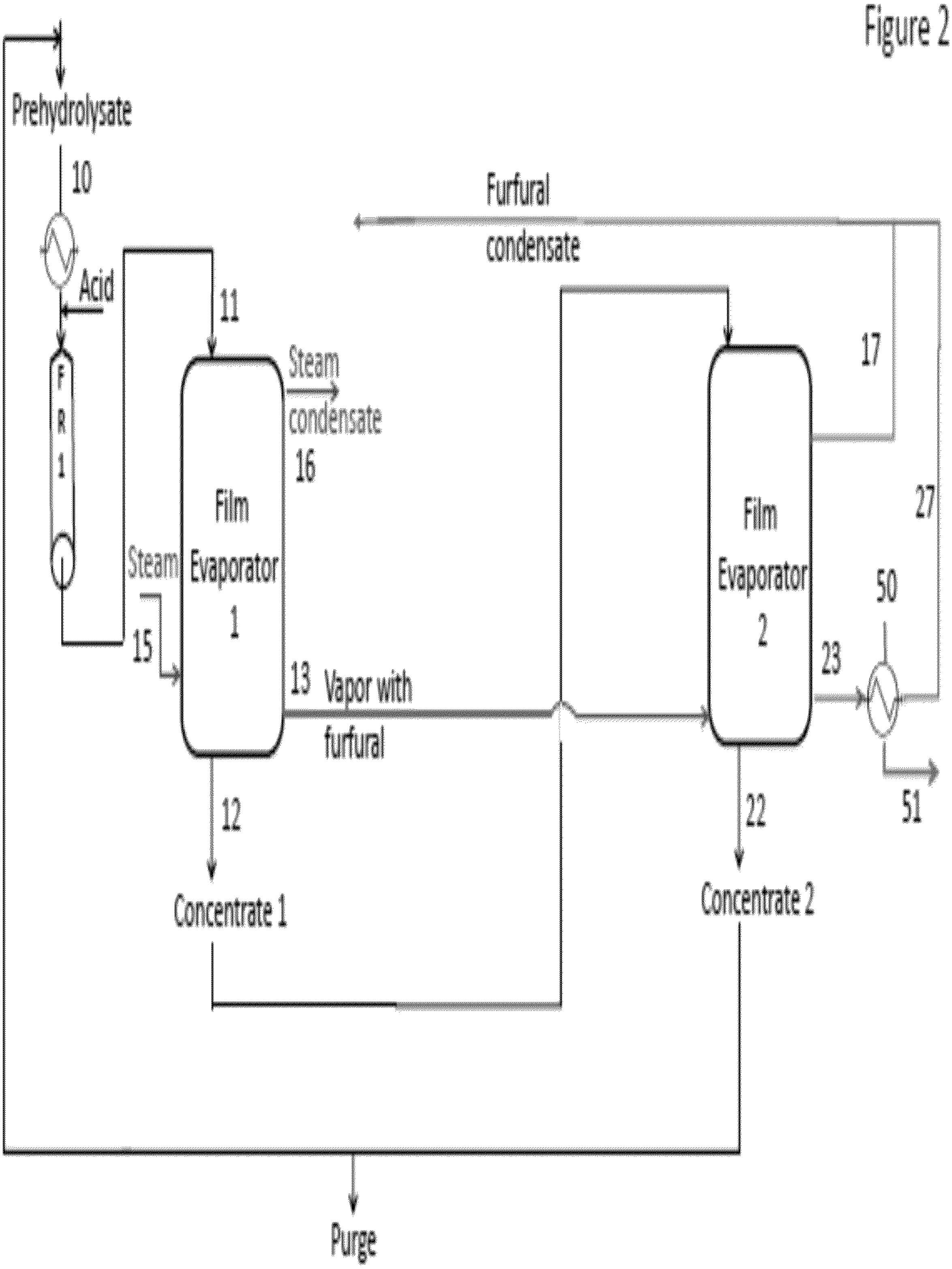
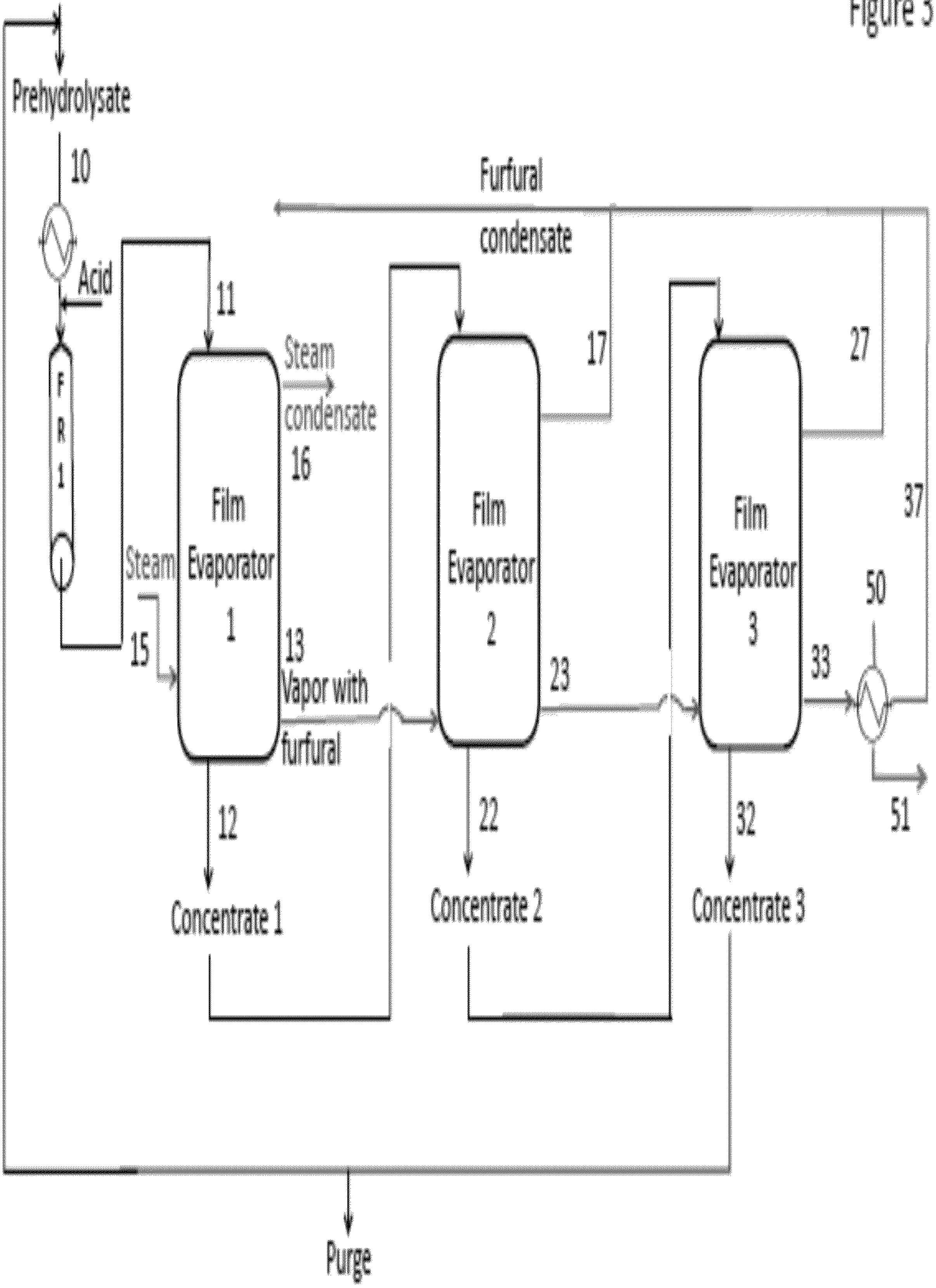

Prehydrolysate
10
Acid
F R 1
11
Steam
condensate
16
Film
Evaporator
1
Steam
15
13
Vapor with
furfural
12
Concentrate 1
Furfural
condensate
17
Film
Evaporator
2
27
50
23
51
22
Concentrate 2
Purge

Figure 3


Prehydrolysate
10
Acid
F R 1
11
Furfural condensate
Steam condensate
16
Steam
15
Film Evaporator 1
13
Vapor with furfural
12
Concentrate 1
17
Film Evaporator 2
23
22
Concentrate 2
27
Film Evaporator 3
33
32
Concentrate 3
37
50
51
Purge

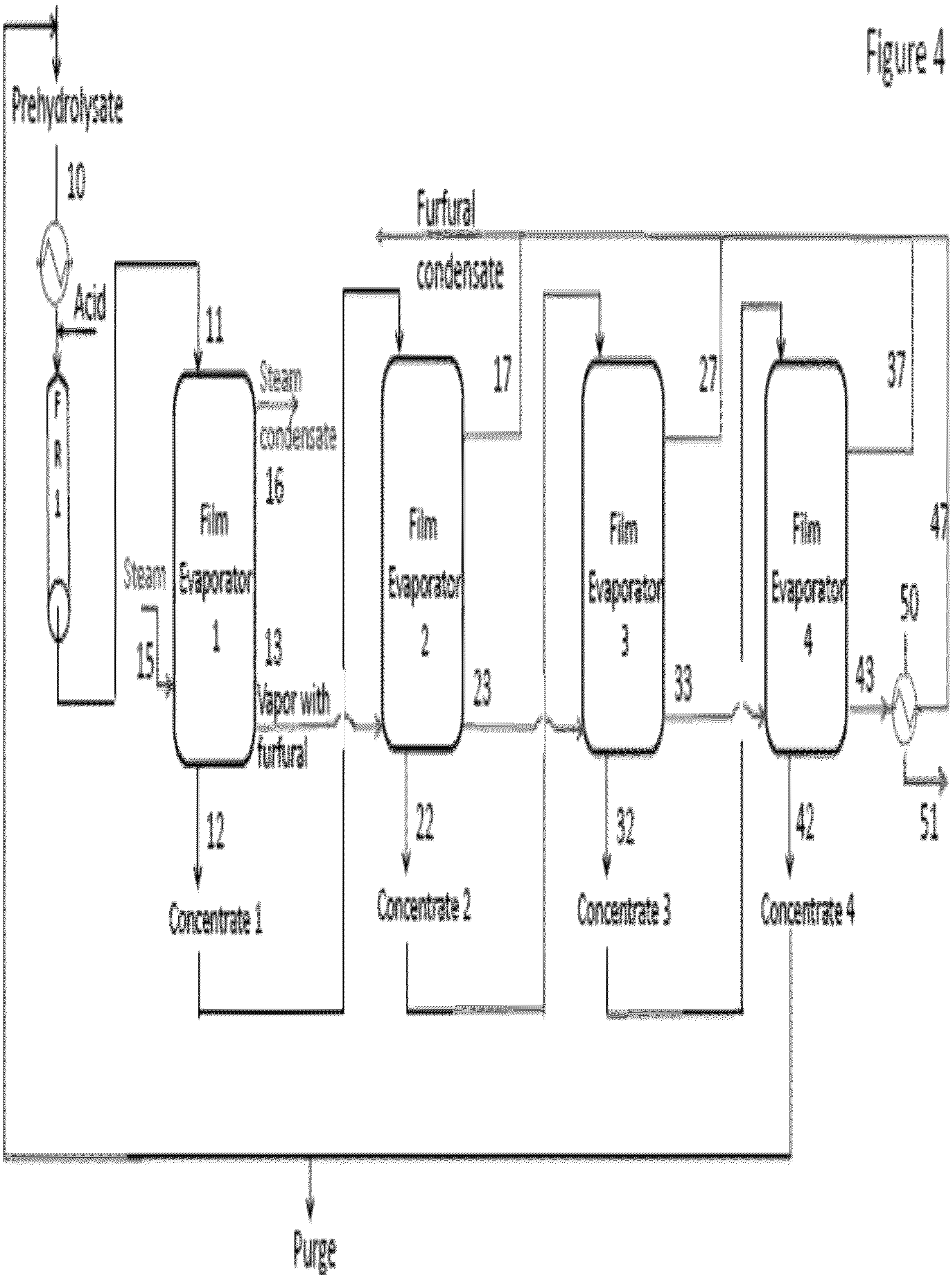
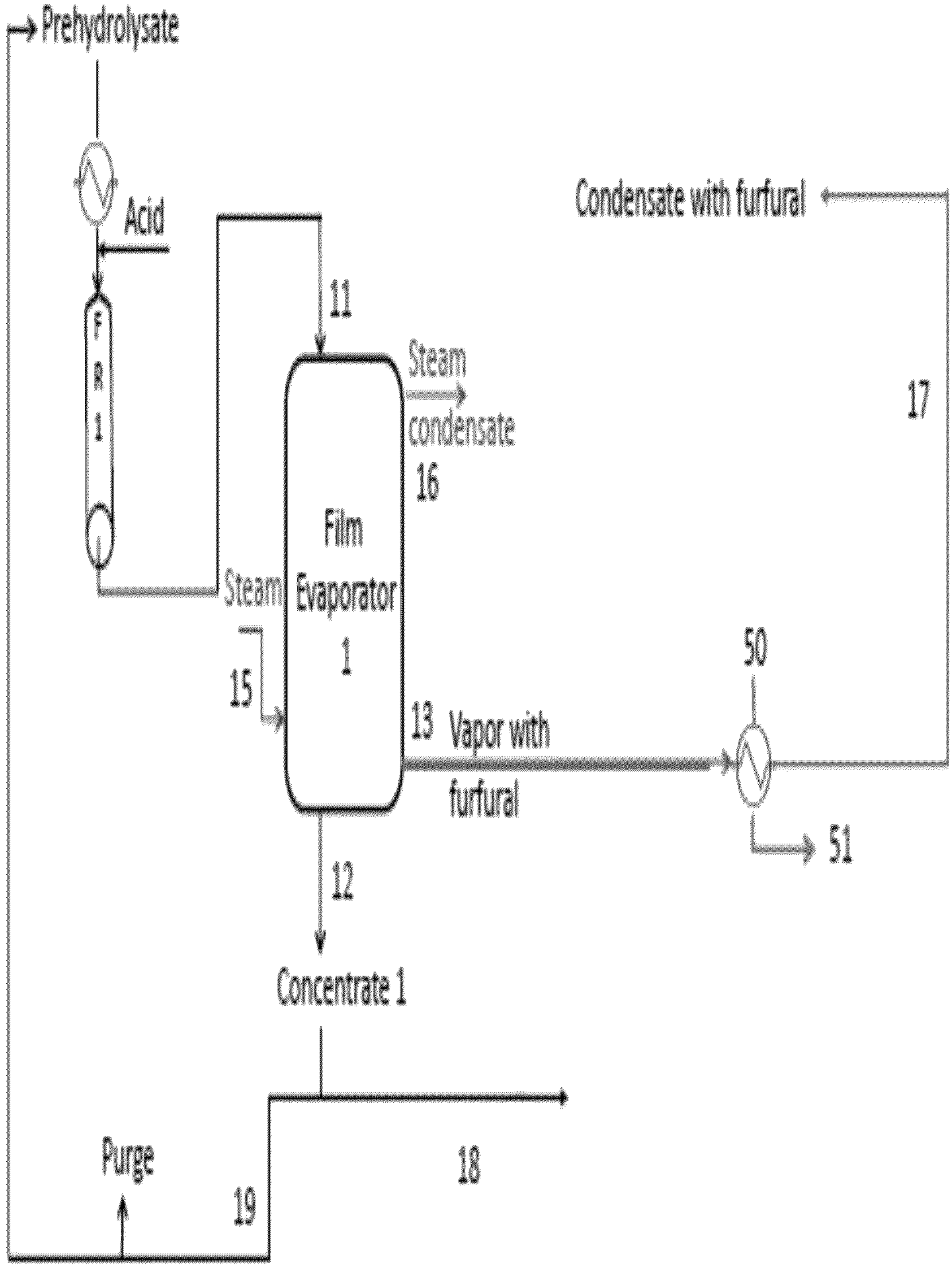


Figure 4
Prehydrolysate
10
Acid
F R 1
11
Steam condensate
16
Steam
15
Film Evaporator 1
13
Vapor with furfural
12
Concentrate 1
Furfural condensate
17
Film Evaporator 2
23
22
Concentrate 2
27
Film Evaporator 3
33
32
Concentrate 3
37
Film Evaporator 4
43
42
Concentrate 4
47
50
51
Purge

Figure 5


Prehydrolysate
Acid
F
R
1
11
Steam
condensate
16
17
Condensate with furfural
Steam
Film
Evaporator
1
15
13
Vapor with
furfural
50
51
12
Concentrate 1
Purge
19
18

INTERNATIONAL SEARCH REPORT

International application No	PCT/EP2024/066415

A. CLASSIFICATION OF SUBJECT MATTER

INV. C07D307/50 C07D307/48 B01D1/22
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C07D B01D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, CHEM ABS Data, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2020/369636 A1 (XU BIN [CN] ET AL) 26 November 2020 (2020-11-26) paragraph [0054]; claim 1 -----	1-24

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

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"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

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"X" document of particular relevance;; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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"&" document member of the same patent family

Date of the actual completion of the international search 5 August 2024	Date of mailing of the international search report 23/08/2024
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Johnson, Claire

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2024/066415

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2020369636 A1	26-11-2020	CA 3083403 A1	13-06-2019
		DK 3722288 T3	10-06-2024
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