

# Recovery of Furfural by using Membrane Technology

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## Abstract

India has agro-based economy and agriculture accounts for a large share of GDP and employment. Besides, a number of useful products, a large quantity of agro-wastes are also produced which is not properly used at present. These agro-wastes are either burnt as fuel or improperly disposed off causing the problem of waste treatment and environmental pollution. Furfural is derived from the pentosan in the cellulose of plant tissues, the most prominent sources of which are corn cobs, saw dust, rice husk, bagasse, pea nut shell. Most furfural that is being produced today is derived from corncobs. In the process we used two different concentrations of sulphuric acid was taken as 14% and 16%. For 16% acid concentration we get maximum conversion of Pentoses to furfural. The hydrolysis process was carried out in simple distillation set up; in distillate we get hydrolysed solution which contained mixture of water, furfural and some light fractions like as methanol acetone etc. After hydrolysis we have to separate furfural from hydrolysed solution therefore we used the Pervaporation process for separation of furfural. Pervaporation is the combination of evaporation and permeation. If we use distillation process after hydrolysis we required maximum time and more energy. By distillation we don't get water, ie water is not recycled. But by pervaporation we get pure water to recycling and required less energy and short duration for process.

**Keywords- Furfural, Pervaporation, Pentosan**

## I. INTRODUCTION

Membrane technology is an evolving separation technology which uses semipermeable membranes to segregate one or more constituents from a mixture [Mulder, 1998]. As a result of the driving force applied to the system the outcomes of the membrane process are the permeate, the part of a mixture that passes through the membrane, and the retentate, the fraction that the membrane retains (Figure 1).

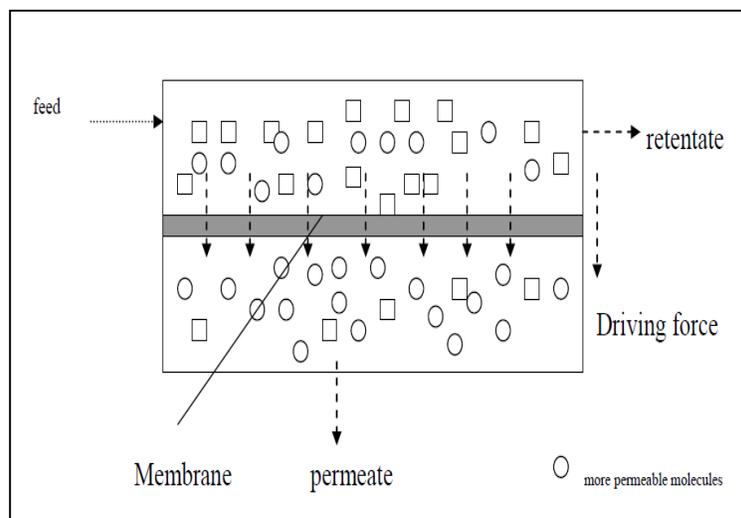


Fig. 1: Schematic diagram of a membrane process

The key feature of this technology is the membrane. There are different definitions of the term membrane. The definition used in this study is “membrane is a perm selective material that allows one or more constituents of a mixture to pass through more readily than others” [Mulder, 1998 and Judd S & Jefferson, 2003]

Depending on the membrane process and application, different membranes are suitable. The performance of a membrane is usually given by the amount of material going through a unit of area of the membrane per unit of time (flux) and the separation effectiveness. The separation effectiveness is measured by several factors among others the selectivity and the enrichment factor. The membrane should exhibit high fluxes and separation effectiveness, and be tolerant to temperature variations and the feed stream components. It should have a low manufacturing cost and display good manufacturing reproducibility [veronica, 2009].

### A. Membrane Classification

Membranes are classified according to different definitions as illustrated in Figure (2). Membranes may be categorized according to the mechanism by which separation is achieved. Porous membranes discriminate according to size of particles or molecules, and dense or non-porous. Membranes discriminate according to chemical affinities between components and membrane materials. In porous membranes the pore can vary from micrometers to nanometers. Membranes may additionally be classified according to the nature of the functional groups comprised in the membrane, into polar or hydrophilic membranes and non-polar or hydrophobic membranes. Hydrophilic membranes preferentially permeate polar compounds, while organophilic permeate non-polar organics.

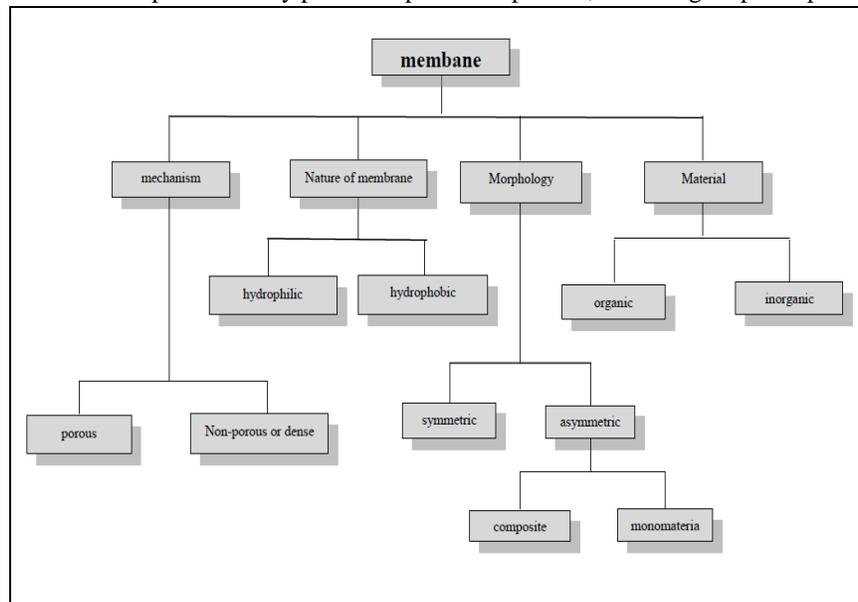


Fig. 2: Classification of membranes according to different criteria

Membranes may also be grouped according to their material composition, which is either organic (polymeric) or inorganic (ceramic or metallic).

Additional membrane categorization is done on the basis of their physical structure or morphology into symmetric or asymmetric. In asymmetric membranes, contrary to symmetric membranes, their pore size varies with the membrane depth. They generally have a thin, dense skin layer supported on a microporous substrate. An asymmetric membrane is formed in either an integral form or in a composite form. The main difference between the two types of asymmetric membranes is whether the skin and the substrate are made from the same polymer material (asymmetric membrane) or not (composite membrane) [Mulder, 1998].

### B. Pervaporation Process

Pervaporation is a separation process in which a liquid feed containing two or more components come into contact with one side of a membrane while vacuum (or purge gas) is applied on the other side to produce a permeate vapor [Fleming, 1992]. It is a promising alternative to conventional energy intensive processes such as distillation and evaporation. It is often referred to as (clean technology), especially for the treatment of volatile organic compound. The separation is not based on relative volatilities as in the case of thermal processes, but rather on the relative rates of permeation through a membrane [Ornthida and somenath, 2010]. In general, pervaporation (PV) can still be labelled as a new technology. Depending on the permeating component two main areas of pervaporation can be identified: (1) hydrophilic PV, and (2) organophilic PV. Figure (3) gives an overview of the areas of PV, membranes applied and application [Frank et al., 1999].

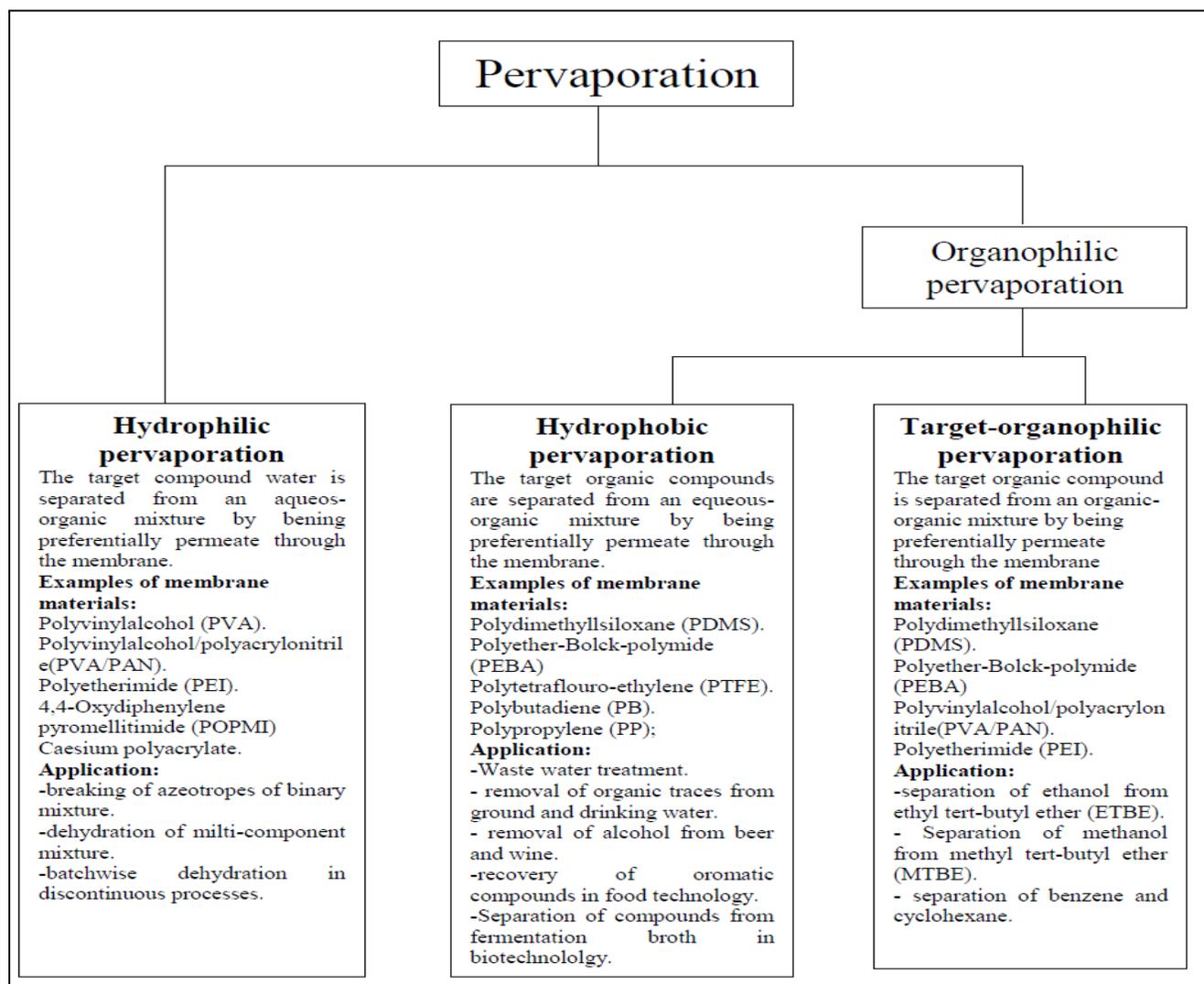


Fig. 3: Areas of pervaporation: membranes and applications [Frank et al., 1999]

## II. PERVAPORATION MEMBRANES

An ideal pervaporation membrane should consist of an ultra-thin defect free skin layer (dense layer) supported by a porous support as shown in Fig (4). The skin layer is perm-selective and hence responsible for the selectivity of the membrane. However, the porous support also plays an important role in overall performance of the membrane. Ideal pervaporation membrane should possess the following characteristics [Anil et al., 2008].

- 1) The top layer/skin should be as thin as possible and without any defects.
- 2) It should exhibit high sorption and diffusion selectivity's for the desired solute when contacted with a mixture containing it.
- 3) It should not swell excessively to maintain the selectivity and structural stability.
- 4) It should possess good mechanical strength, chemical and heat stability.
- 5) It should offer high fluxes without compromising selectivity.

The thin dense layer of composite pervaporation membranes is coated on a substructure consisting of a porous support membrane with an asymmetric pore structure and a carrier layer of woven or non-woven textile fabric. The thin dense layer or separating layer defines the type of composite membrane and thus the nature of the separation. The separating layer may be hydrophobic or hydrophilic according to the functional groups of the membrane material [veronica, 2009].

The porous support under the organic separating layer is made of structural polymers such as polyacrylonitrile, polyetherimide, polysulfone, polyethersulfone, and polyvinylidene fluoride [Bruschke, 2001]. Ideally, the porous substrate presents negligible resistance to mass transport [Koops et al., 1993]. Otherwise, the substrate resistance leads to decreased membrane productivity and selectivity [Pinnau & Koros, 1991].

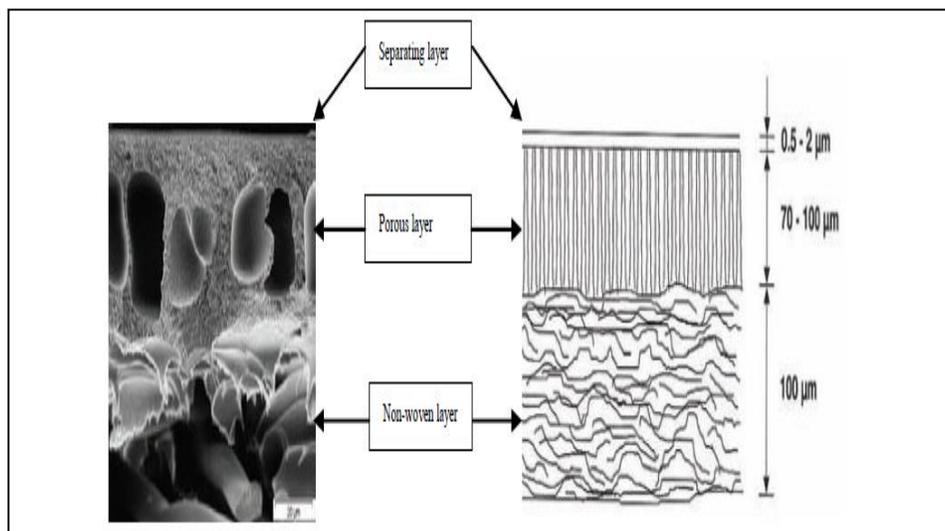


Fig. 4: Cross-section of a composite membrane [veronica, 2009, Koltuniewicz & Drioli, 2008]

Pervaporation membranes may also consist of dense homogeneous polymer films. Such membranes show high selectivities in the separation of liquid mixtures. However, they exhibit low fluxes due to their high thickness (50– 250  $\mu\text{m}$ ) [Dotremont, 1994 and Zereshki et al., 2010]

### III. METHODOLOGY

Corn cobs used for the synthesis of furfural which are contains

Cellulose  $\square$  32.3 - 45.6%,

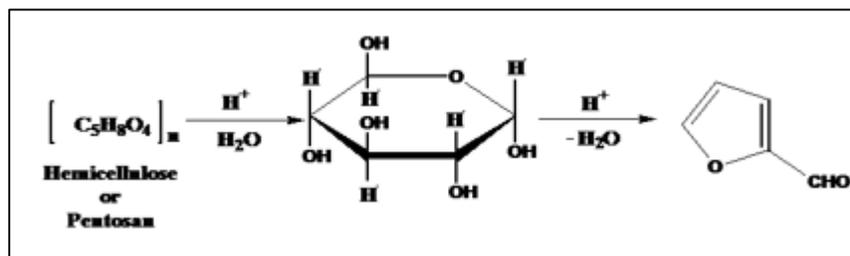
Hemicelluloses  $\square$  39.8%, Lignin  $\square$  6.7 – 13%

Corn cobs have been used on a small scale as a fuel for direct combustion in cooking and heating. Corn cobs are not harvested, stored, or utilized in a moisture free condition. Use of corn cobs as a biomass feedstock offers promising possibilities for renewable energy production. Corn cobs have a bulk density of about pounds per cubic foot and may be stored economically in the open in a cheap wire-fenced enclosure. Cobs are of little commercial value, but because the gain is generally shelled at individual farms or certainly in scattered rural areas, collection and transportation of cobs to the manufacturing plant becomes a major consideration of cost. Some 12,000tons per annum of cobs would be required to produce 1,000tons of furfural per annum. It would seem therefore that corn cobs alone would never entirely fulfill raw material demands. The methodology of synthesis of furfural is contains Pretreatment Process, Hydrolysis, Separation Processes, Purification Processes.

After hydrolysis we have to separate furfural from hydrolyzed solution therefore we used the Pervaporation process for separation of furfural. Pervaporation is the combination of evaporation and permeation. In this process we have used PV apparatus in which PTFE (polytetrafluoroethylene) membrane of 0.2 $\mu\text{m}$  pore diameter and the cross section area is found 5.06 $\text{cm}^2$ .



Fig. 5: Pervaporation process

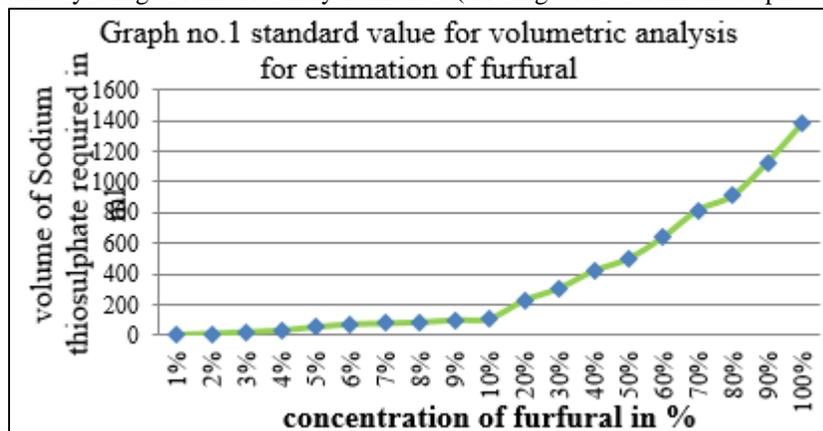


The hydrolyzed solution fed to the flask of PV apparatus then temperature is increased up to 50-80°C and then vacume pump is started and permeation of furfural is carried out 2mm.hg. because PTFE is Hydrophobic membrane which is only organophilic. This operation is carried out upto 30min -1hr. After permeation we condensed the Vapour of Furfural and we get product furfural in pure form.

Corncob is alignocellulosic material which contained 37% of hemicellulose which highly compact with pentoses. Corncob contains 30% of pentoses of total composition and after hydrolysis it converted in to furfural. In above process we have used 500grams of corn cob as a raw material in each time. The temperature for hydrolysis was also taken constant as 120°C and time for hydrolysis was also same for each batch as 100minute.

#### IV. RESULTS

In above process we used two different concentrations of sulphuric acid was taken as 14% and 16%. For 16% acid concentration we get maximum conversion of Pentoses to furfural. The hydrolysis process was carried out in simple distillation set up; in distillate we get hydrolysed solution which contained mixture of water, furfural and some light fractions like as methanol acetone etc. the maximum concentration of furfural was found as 9.2% by using 16% H<sub>2</sub>SO<sub>4</sub> acid. The confirmation of furfural concentration in hydrolysed solution was done by using volumetric analysis method (titrating with sodium thiosulphate).



Graph 1: standard value for volumetric analysis for estimation of furfural

In this method we confirm the concentration of furfural in given solution. In this we took 5ml of sample was measured into a conical flask and 4ml of 0.05M potassium bromate/bromide (KBrO<sub>3</sub>/ KBr) solution added and allowed to stand for 5 minutes. 2ml of 5% (0.05M) potassium iodide (KI) was then added and the liberated iodine titrated with a standard 0.1M sodium thiosulphate (Na<sub>2</sub>SO<sub>2</sub>.5H<sub>2</sub>O) solution. Then the readings recorded and same process carried out for blank experiment. In above graph we have found the standard values of sodium thiosulphate required for different known concentration. From above graph characteristics we can say that if we increase the concentration of furfural then the volume of sodium thiosulphate required is also increased. By using above standard graph we can calculate concentration of furfural by knowing value of sodium thiosulphate required.

##### A. For Pervaporation Process

After hydrolysis we have to separate furfural from hydrolysed solution therefore we used the Pervaporation process for separation of furfural. Pervaporation is the combination of evaporation and permeation. In this process we have used PV apparatus in which PTFE (polytetrafluoroethylene) membrane of 0.2µm pore diameter and the cross section area is found 5.06cm<sup>2</sup>. The hydrolysed solution fed to the flask of PV apparatus then temperature is increased up to 80°C and then vacume pump is started and permeation of furfural is carried out 267Pa.(2mm.hg.) because PTFE is Hydrophobic membrane which was only organophilic. This operation was carried out up to 1Hr. then we get mixture of furfural and light fractions like methanol acetone etc. From above observation table we could say that if we increased the feed concentration then the concentration of furfural in permeates also increased. In this process we get pure water in rejected. After that mixture was fed to distillation process.

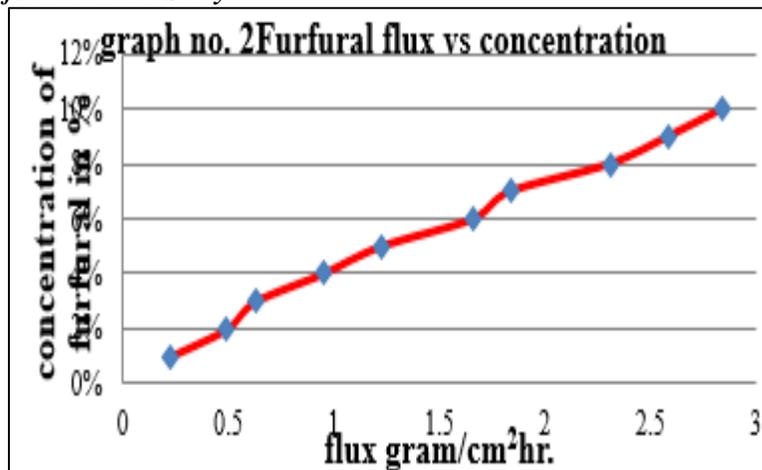
**B. For Distillation of Pervaporated Solution**

After pervaporation we get a mixture of light fractions and furfural. For purification of furfural we used the process of simple distillation. This process was carried out for only 30 minute and 120°C. Pure furfural was got as a residue and in distillate we get light fraction mixture. After whole process we confirmed concentration of furfural by using above volumetric estimation process. From which we get the maximum concentration of furfural as 99%. In above process we took the temperature of 120°C because all light fractions were distilled and we get pure furfural.

**C. For Distillation of Hydrolyzed Solution**

For comparatively study of double distillation and pervaporation we had distillate the hydrolyzed solution after hydrolysis. In the above observation we took 200ml of hydrolyzed solution for distillation at different initial concentration. The distillation time was 2Hr. and temperature at 120°C. Then we get mixture of water and light fractions in distillate and mixture of water and furfural in residue. For further purification we need redistilled to above mixture of water and furfural so we also need more energy for purification of furfural. In above process we were found maximum concentration of furfural in residue as 65 %. And in distillate we were get mixture of water and light fractions for further separation we need redistilled it. So above process was more energy demanding process. While from table no.2 and 3 we can say that if we done the pervaporation of hydrolyzed solution then we get mixture of furfural and light fractions in permeate and pure water in reject. The concentration of furfural in permeate was found 55%-59%. The process of pervaporation was carried out at 80°C for 1 hr. after pervaporation we take permeate solution for distillation at 120°C for 30 min only then we got in distillate light fractions and in residue we got 95-99% pure furfural. Therefore if we use distillation process after hydrolysis we required maximum time and more energy. By distillation we dont not get water, in separated form means ie water is not recycled. But by pervaporation we get pure water to recycling and required less energy and short duration for process.

**D. Pervaporation Process for Parameter Study**



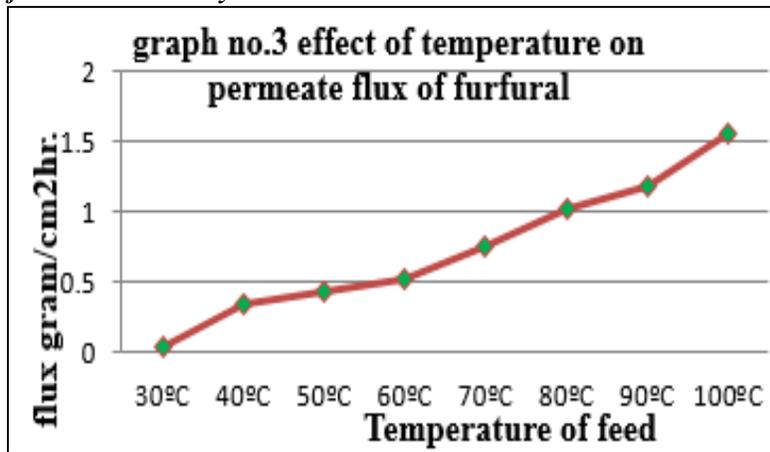
Graph 2: Furfural flux vs concentration

For study of different parameter we were carried out the pervaporation process for different condition in above case we used same quantity of feed, constant temperature of pervaporation and constant time for process. In above case we was taken different initial concentrations of furfural and fed to pervaporation set up. After pervaporation we get quantity of furfural in permeate and measured the flux rate of furfural permeation through PTFE membrane. From above observation we can say that if we increased the concentration of furfural in feed then the flux rate also increased. For denoting the effect we draw the graph between the feed concentration and flux rate of furfural permeation.

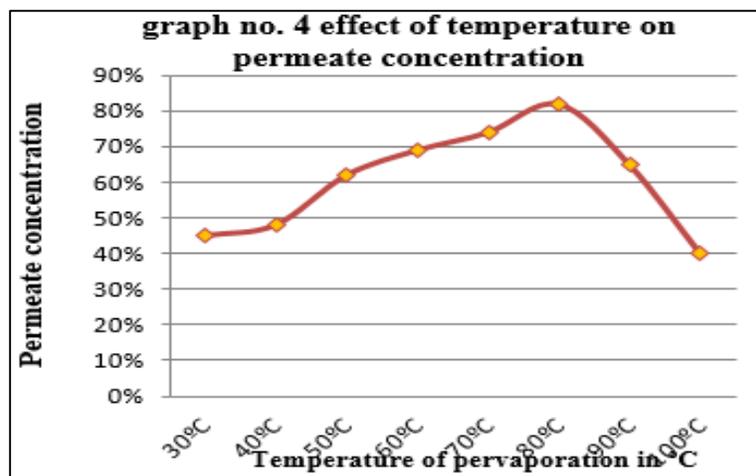
$$\text{flux} = \frac{\text{weight of permeate quantity in grams}}{(\text{time required to permeate in Hr.}) \times (\text{cross section area of membrane})}$$

From above formula we can calculate flux of furfural permeation through PTFE membrane. Time was same 1hr and the cross sectional area of membrane was 5.06cm<sup>2</sup>. In graph no.2 the graph characteristics we can say that if we increase the concentration of furfural in feed then flux of furfural permeate is also increased proportionally. We were taken maximum concentration of furfural in feed 10% for that we get flux rate of 2.8458 gram/cm<sup>2</sup>hr.

E. Pervaporation Process for Parameter Study

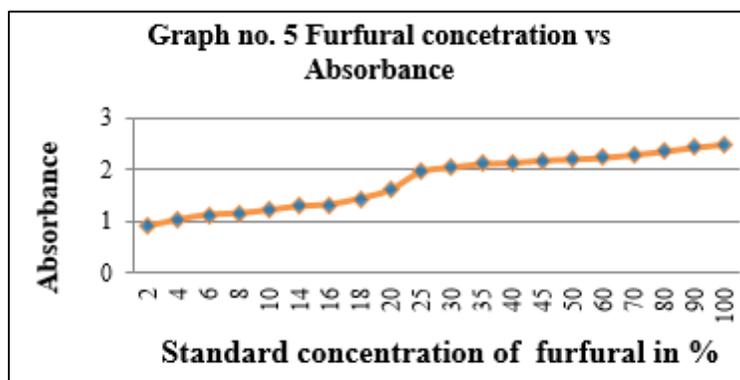


Graph 3: Effect of temperature on permeate flux of furfural



Graph 4: Effect of temperature on permeate concentration

For study of different parameter we were carried out the pervaporation process for different condition in above case we used same quantity of feed, constant initial concentrations of feed and constant time for process. In above case we were taken different temperature of pervaporation. After pervaporation we get quantity of furfural in permeate and measured the flux rate of furfural permeation through PTFE membrane. From above observation we can say that if we increased the temperature of pervaporation then the flux rate also increased. For denoting the effect we draw the graph between the temperature of pervaporation and flux rate of furfural permeation. From above graph no. 3 characteristics we can say that if we increase the temperature of pervaporation then we get increased in permeate flux of furfural through PTFE membrane. The maximum flux rate gets at 100 °C. From above graph no.4 characteristics we can say that if we increase the pervaporation temperature then the permeate concentration of furfural through PTFE membrane is also proportionally increased up to 80 °C after that the permeate concentration was decreased because after 80 °C the water Vapour will gets increases and then nature of membrane turns into hydrophilic and concentration of furfural gets decreased.



Graph 5: Furfural concentration vs Absorbance

## V. CONCLUSION

Furfural was synthesized by acid hydrolysis process & its separation was done by using membrane separation techniques. In this work different parameters like effect of feed composition on permeation flux, effect of feed composition on furfural concentration in permeate, effect of temperature on permeate flux, effect of temperature on furfural concentration. Comparatively use of PV for the separation and high quality of furfural yield by using PTFE membrane also done. It can be thus concluded that if we increase the temperature of feed then the permeate flux through membrane is increased. It is a promising alternative to conventional energy intensive processes such as distillation and evaporation. It is often referred to as (clean technology), especially for the treatment of volatile organic compound. The separation is not based on relative volatilities as in the case of thermal processes, but rather on the relative rates of permeation through a membrane.

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