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# Processes Separation to Furfural, Design and Optimization Involving Economical, Environmental and Safety Criteria

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## Abstract

In this work is presented the simultaneous design and optimization of three alternatives of azeotropic distillation processes to purify Furfural by the mathematical technique called Differential Evolution with Tabu List (DETL), having as objective functions economic, environmental and safety criteria to the processes were evaluated. The schemes here studied are: conventional Quaker Oats process to purification of Furfural (CQO), an azeotropic distillation process with heat integration through vapour recompression (DHI) and dividing wall azeotropic distillation column (DWC). The results of the simultaneous optimization show that the intensification processes DHI and DWC have important reduction on the cost and environmental impact, with respect to conventional process (CQO). However, the increase in operative pressures in the case of DHI process and the increase of internal flows and the size of equipment in DWC process cause an increment of the risk, despite of the risk increment in DWC it is considered the best option to furfural purification due reductions mainly on TAC and Eco99 that mean important savings in a long-term.

**Keywords**: Furfural, Optimization Process, Multi- Objective Optimization, Process Intensification, Bio-Refinery.

## 1. Introduction

The depletion of sources energy, greenhouse effect and the high environmental impact, are some problems of using petroleum. Thus the efforts in recent years have been focused on developing of alternative renewable resources that can replace to derivate petroleum products like fuels, plastics among others. The biomass is considered the most important among the renewable resources due to is the most abundant feedstock in the planet (Long et al. 2016). The US National Renewable Energy Laboratory (NREL) gave himself to the task to identify the chemicals from biomass and listed 30 potential chemical from biomass that could compete and replace the chemical from petroleum. Furfural stands out in this list with a wide range of applications that go from extracting for the refinement of lubricating oils, as a fungicide, nematocide and as a raw material (up to 65% of all furfural produced), to furfural alcohol production and other important products like levulinic acid (Long et al. 2016).

The furfural is produced from biomass rich in pentoses like corn cobs, oat hulls, sugar cane bagasse to name a few. The first process production of furfural was Quaker Oats process stablished in 1921 and it remains as the most used today. This process has had few changes since 1921, the Quaker Oats consists mainly of two steps, which are a reaction and distillation steps respectively. At the reaction step, the biomass is pretreated and subsequently it is introduced in a reactor with diluted sulphuric acid where the biomass is degraded in a hydrolysis reaction into furfural, methanol and acetic acid. The stream from the reactor has a composition in mass fraction of 6% furfural, 4% of methanol and acetic acid and 90% of water (Zeitsch; 2000). As almost all bio-refinery process, the low composition of the main product (in this case furfural) conditions us to high separation costs, in the case of furfural purification these costs are even higher due the formation of azeotropes between the organic components with the water. For this reason in this work are studied three different azeotropic distillation process to purify Furfural; conventional Quaker Oats process purification of Furfural (CQO) and two intensifed processes, an azeotropic distillation process with heat integration through vapour recompression (DHI) and dividing wall azeotropic distillation column (DWC). Due the bio-refineries need to be the most profitable and cheap, with less environmental impact and with the safest operating conditions, the design and optimization of the three distillation process were realized in order to minimize these aspects.

## 2. Methodology

The three different schemes studied in this work are showed on the Figure 1, compositions and flows were taken by Long et al. 2016. The CQO and DHI processes consist in an azeotropic column (C1) that breaks the azeotrope furfural-water, a mixture rich in water and acetic-acid leaves the bottom of this column, whereas from the top of the azeotropic column a stream rich in water and methanol leaves the column, which is then separated in a conventional distillation column (C2), also a side stream is withdrawn between the top and bottom of C1, this stream contains a mixture rich in water and furfural which is sent to a decanter where the organic phase rich in furfural is purified in a third column (C3). On the other hand the DWC process, the C1 and C2 have been integrated in only one column with a dividing wall.

The three distillation schemes were designed and simulated using ASPEN PLUS$^{TM}$ to obtain purities of 99.2% and 99.5% mass fraction of methanol and furfural respectively. The vapor-liquid equilibrium can be predicted by NRTL-HOC model, which includes the Hayden- O´Connell equation, which can predict reliably the solvation of polar compounds and dimerization in the vapor phase, which occurs with mixtures containing carboxylic acids (Long et al. 2016).

The total annual cost (TAC), Eco-indicator 99 (Eco99) and individual risk (IR) were chosen as the objective function to be minimized. TAC was calculated through the Guthrie method, all the parameters for the equipments were taken from Turton et al. 2008, carbon steel was the assumed as the construction material for all the equipments, and the time of investment was considered ten years. The trays selected to the columns were the type Sieve with spacing between trays of 2 ft. The operating costs included cooling utilities, heating utilities, and 8500 hours of yearly operation for each configuration were defined. The operating costs were taken of Turton et al. 2008.

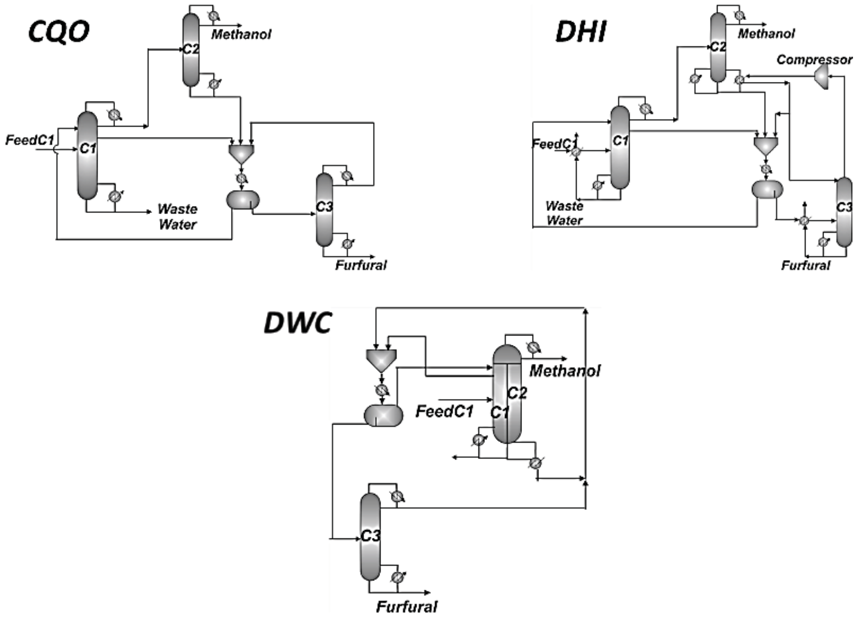


*Figure 1. Azeotropic Distillation schemes to furfural purification*

The Eco99 was used to evaluate the sustainability of the processes, this methodology is based on lifecycle analysis of different categories where individual scores are assigned depending on the categorie, three impact categories (steel, electricity, and vapor) were considered according to work presented by Errico et al. 2016 where this indicator has been utilized to quantify the enviromental impact in some chemical processes. In the case of the safety, the individual risk was calculated through quantitative risk analysis technique, which is a methodology of inherent safety where the main objetive is to evaluate the frecuency and probability of decease or injury due to accidents like explotions or toxic release. This metodology has been succesfully used to evaluate the risk on chemical process (American Institute of Chemical Engineers 2000), the equations and procedure was realized to a distance of 50 m from the equiments according to reported by American Institute of Chemical Engineers, 2000.

In this work, it has been used the Differential Evolution with Tabu List Algorithm which is a multi-objective optimization method proposed by Sharma and Rangaiah 2010. The DETL has four basic steps: generation of initial population, mutation, crossover, a selection of the best solutions, each one of these steps require of some parameters that need to be determined by a tuning process where is evaluate the ability of the algorithm the algorithm's ability to find solutions that meet all constrains. The value of required parameters to the DETL algorithm determinate by tunning process are the following: Population size (NP): 120 individuals, Generations Number (GenMax): 834, Tabu List size (TLS): 60 individuals, Tabu Radius (TR): 0.01, Crossover fractions (Cr): 0.8, Mutation fractions (F): 0.3. The implementation of the multi-objective optimization strategy involved a hybrid platform, which linked Aspen Plus$^{TM}$, Microsoft Excel$^{TM}$. The decision variables for each reactive distillation configuration are reported in Table 1. Finally, the multi-objective optimization problem can be expressed mathematically as in Eq. (1) and Eq. (2):

$$\min \quad Z = \{TAC; Eco99; IR\} \tag{1}$$

Subject to:
$$\begin{aligned} y_{i,PC} &\geq x_{i,PC} \\ w_{i,FC} &\geq u_{i,FC} \end{aligned} \tag{2}$$

Table 1. Decision variables of the reactive distillation configurations.

| Decision Variables | Continuous | Discrete |
|---|---|---|
| Number of stages, C1 | | X |
| Number of stages, C2 | | X |
| Number of stages, C3 | | |
| Feed stage recycle of C1 | | X |
| Feed stage, C1 | | X |
| Stage of side stream C1 | | X |
| Feed stage C2 | | X |
| Feed stage C3 | | X |
| Reflux ratio of C1 | X | |
| Reflux ratio of C2 | X | |
| Reflux ratio of C2 | | |
| Heat duty of C1, kW | X | |
| Heat duty of C2, kW | X | |
| Heat duty of C3, kW | | |
| Diameter of C1, m | X | |
| Diameter of C2, m | X | |
| Diameter of C2, m | X | |
| Discharge pressure of compressor(Comp), atm | X | |
| Interlinking flow, Kg $h^{-1}$ | X | |

The objective function is restricted to the accomplishment of the purity vectors, and the mass flowrate vectors for the components in the mixture. For example, the values of the purities for the components obtained during the optimization process $y_{i,PC}$ must be either greater or equal to the specified values of purities for the component $x_{i,PC}$. Furthermore, the mass flowrates obtained $w_{i,PC}$ must also be either greater or equal to the specified values of the mass flowrate $u_{i,PC}$.

## 3. Results

The optimal design parameters, design specifications, and values for the objective functions for all the studied sequences are offered in Table 2. Figure 2 shows the Pareto charts of the DWC process, the DHI and CQO keep the same tendency.

The results show that the DHI process does not provide a big saving of TAC and the values of Eco99 and IR are bigger than the values of the CQO process. The reason of these results is because the energy savings in DHI are very low compared to conventional process, the addition of more equipment such as heat exchangers and compressors directly affects steel category on Eco99 and the probability of an accident to occur increases due IR value is bigger than CQO.

Table 2. Optimal design parameters for the sequences.

| Design Variables | CQO | DHI | DWC |
|---|---|---|---|
| Number of stages, C1 | 50 | 51 | 70 |
| Number of stages, C2 | 9 | 33 | 72 |
| Number of stages, C3 | 6 | 8 | 12 |
| Feed stage recycle of C1 | 14 | 19 | 5 |
| Feed stage, C1 | 30 | 29 | 37 |
| Stage of side stream C1 | 12 | 13 | 30 |
| Feed stage C2 | 8 | 20 | ------ |
| Feed stage C3 | 4 | 7 | 6 |
| Reflux ratio of C1 | 22.95 | 2.93 | ------ |
| Reflux ratio of C2 | 0.203 | 1.25 | 25.09 |
| Reflux ratio of C3 | 1.564 | 0.28 | 0.273 |
| Heat duty of C1, kW | 20018 | 19519 | 19131 |
| Heat duty of C2, kW | 773 | 882 | 320 |
| Heat duty of C3, kW | 604 | 566.246 | 715 |
| Diameter of C1, m | 1.396 | 0.86 | ------ |
| Diameter of C2, m | 0.524 | 0.80 | 1.535 |
| Diameter of C3, m | 0.380 | 1.13 | 0.321 |
| Discharge pressure of compressor(Comp), atm | ------ | 1.29 | ------ |
| Interlinking flow, kg $h^{-1}$ | ------ | ------ | 25887 |
| TAC ($/yr) | 9,383,987 | 9,318,611 | 9,179,222 |
| Eco99 (Eco-points) | 4,344,805 | 4,546,195 | 4,299,778 |
| IR (1/yr) | $2.734\text{x}10^{-4}$ | $2.850\text{x}10^{-4}$ | $5.371\ \text{x}10^{-4}$ |

In the case of DWC this process has savings of TAC and low Eco99 value with respect to CQO process due there are less equipment because of the thermally coupling. This process presented an important reduction in the side of the divided wall column that corresponding to column C2 in the conventional process, however the column C3 has an increment in the energy consumption of around 100 KW with respect to the C3 column of CQO process. The azeotropic column is the equipment that contributes with the greatest amount of energy in the CQO process, the DWC has a reduction near 900 KW it indicates that TAC and Eco99 reductions are due the lessening of steel category because of the integration of C1 and C2 columns in only one equipment and it is not for energy savings. The IR presents increment in DWC process with respect to CQO, the increment of risk is mainly due the increment of the size and the amount of material of dividing wall column. The IR is dependent of the size of equipment, bigger distillation columns imply that there is more mass inside the columns from which like explosions can derivate in a greater range of damage , and due DWC is used to purify methanol, a big column represents more flammable material inside it, then the potential of a more destructive accident increases. It has traditionally been thought that dividing wall columns provide more secure process due to the reduction of equipment reduce the probability of accident, nevertheless, the results obtained in this work indicate that this affirmation may not be met in all cases.

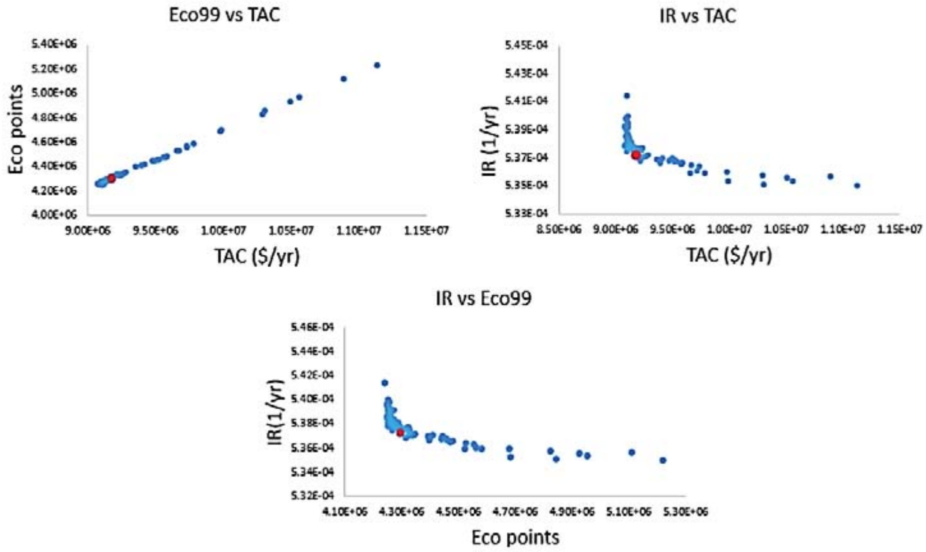


*Figure 2. Pareto Fronts to DWC process*

## 4. Conclusions

In this work was realized the simultaneous design and optimization of three alternatives to purification of furfural, the application of the quantitative risk analysis represents an additional selection criterion that can help to take measures to a safe operation of these processes. The results indicate that the DHI does not provide reductions on TAC, Eco99 and IR compared to CQO processes thus DHI is not considered a good option to purify furfural. The DWC processes has an increment in the value of IR compared with CQO mainly to increase in size of dividing wall column, we considered that IR of DWC process is not enough large to a dangerous. Therefore, DWC is considered the best option to furfural purification due reductions mainly on TAC and Eco99 that significates important savings in a long-term.

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