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Optimised Separation Process of Ketones from Biomass Pyrolysis Oil

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With the growing environmental awareness, renewable energy sources that can replace crude oil are being in-depth studied. One of these is the bio-oil, a renewable energy source that can be obtained from biomass pyrolysis. It is characterised by the fact that its components include ketones, furans, and phenols. Among the ketones, cyclopentanone, 2-butanone, and 2,3-butanedione are the most significant, as they are useful for producing fine chemicals. The first objective of the present study is the design of a suitable separation process for the mixture composed of cyclopentanone, 2-butanone, and 2,3-butanedione, considering the presence of an azeotrope between the 2-butanone and 2,3-butanedione. For this purpose, the enhanced distillation method of pressure-swing distillation is used. To the best of our knowledge, this technique has not been applied before for this particular separation, as existing studies consider the mixture as ideal and do not take into account the presence of the azeotrope. Therefore, the separation process becomes simpler. The second objective is to optimise the aforesaid process. Given the combination of real and integer variables, the high dimensionality of the problem and the constraints on the variables, it has been decided to apply a genetic algorithm as an optimisation method. The optimised variables are the number of stages and reflux ratios of the columns, the molar flow rate of the recirculation stream and the pressure of the high-pressure column. The genetic algorithm is implemented in MATLAB ® programming language, and rigorous simulations are performed using Aspen Plus ®. The optimised variables and compositions of all streams are determined; the results of the overall heating services are 12,788 kW, and cooling services are 12,512 kW for 100 kmol/h of the crude feed. By improving the process of compound separation from pyrolysis bio-oil, the present study contributes to the use of renewable resources such as biomass instead of crude oil to produce valuable chemical compounds.

1. Introduction

Fossil fuels (coal, crude oil, and natural gas) generate 81 % of the primary energy supply. Renewable energy sources, including solar, wind, hydro, and biomass, comprise only 13.8 % of the primary energy supply (Global Bioenergy Statistics, 2020). Renewable biomass is a likely candidate to supplement and replace fossil oils for transportation fuels, chemicals, and materials in petroleum-based industries. Municipal solid waste is also an important source of producing bio-oil. Hoang et al. (2022) have studied its use to achieve a circular economy, as well as some methods to achieve its application to the industrial level.
Compared with coal, some of the advantages of biomass are its sustainability when properly managed, high reactivity in biological conversion processes, and a high potential for bio-oil production due to its oxygen content (Fang et al., 2020). A way to benefit from the biomass energy potential is through the pyrolysis process, which is the thermal decomposition of organic material in the absence of oxygen, leading to the formation of liquids, gases, and highly reactive carbonaceous char. Lower process temperatures favour the production of charcoal, whereas high temperatures increase the gas yields. Pyrolysis processes are divided into three types: slow, fast, and flash pyrolysis. The liquid product, known as bio-oil, is characterised by presenting differently sized molecules with a large amount of oxygen (in contrast to petroleum fuels). Among the functional groups, hydroxy-aldehydes, hydroxy-ketones, and sugars are included (Pandey, 2008). Within the ketones group, cyclopentanone, 2-butanone, and 2,3-butanedione are the most significant ones, as they can be used as raw

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materials to produce fine chemicals. 2-butanone is the second most important ketone, primarily used as a solvent for paints and adhesives, as well as an activator for some oxidative reactions (Ullmann, 2011a). Cyclopentanone is used in the production of cyclopentylamine (used as an intermediate for the potato and rice fungicide pencycuron). Some of its derivatives are important as fragrance materials. It is also used as a solvent for polycarbonates. 2,3-butanedione is used in low quantities as a flavour component for ice creams, baked goods, and perfumes (Ullmann, 2011b).

Distillation is the main unit operation used to separate mixtures. However, the mixture of cyclopentanone, 2-butanone and 2,3-butanedione presents a binary azeotrope, and in consequence, an enhanced distillation must be used to achieve the complete separation.

Recently, Shang et al. (2022) obtained liquid-vapour equilibrium data for this mixture, but unfortunately, their study did not consider the presence of a binary azeotrope between 2-butanone and 2,3-butanedione, treating the mixture as ideal. In consequence, the separation is achieved with two conventional distillation columns. They also simulate the process but without carrying out its optimisation. The present study analyses how the presence of the azeotrope affects the separation procedure. Considering the non-ideality of the mixture, an enhanced distillation must be implemented in order to separate the mixture.

Pressure-swing distillation (PSD) is an enhanced distillation method to separate azeotropic mixtures. It relies on the fact that the composition of the azeotropes is pressure-dependent, in such a manner that when changing the pressure, the mixture can jump to the other side of the azeotrope (Kiss, 2013). PSD prevents the problem of introducing a third component and has gained a lot of attention from researchers in recent years compared to other enhanced distillation methods.

The aim of the present study is to design and optimise the separation process of the azeotropic mixture cyclopentanone, 2,3-butanedione and 2-butanone through a PSD system. To do this, a base simulation template is simulated using Aspen Plus ® and then optimised using a genetic algorithm implemented in MATLAB ® programming language, which allows a continuous link and flow of information with Aspen ® software. The variables to be optimised are the number of stages and the feed stage, reflux ratios, molar flow of the recirculation stream and the pressure of the pressurised column. The objective function is the Total Annual Cost (TAC), given by Luyben (2012) cost correlations.

2. Materials and methods

2.1 Separation process design

Considering the experimental data of the binary systems obtained by Shang et al. (2022) and estimating the missing data using UNIFAC model, the ternary diagram of the mixture at 1 atm is presented in Figure 1.

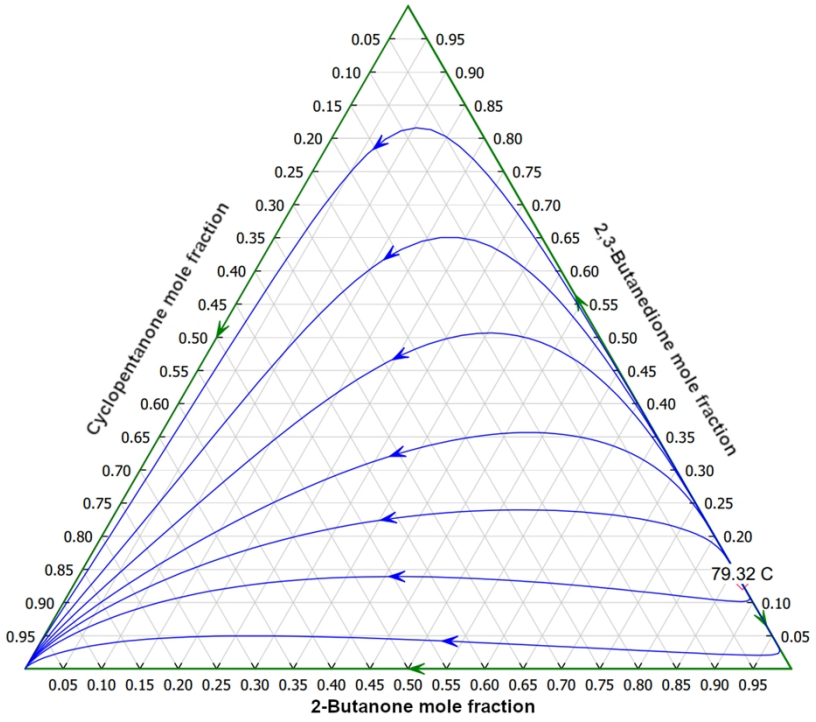

Figure 1: Ternary diagram for cyclopentanone, 2-butanone and 2,3-butanedione mixture at 1 atm

A binary azeotrope between the 2,3-butanedione and 2-butanone boiling at 79ºC hinders the separation. Consequently, to separate the three components, an enhanced distillation is required. According to Figure 2, in the binary diagram of 2,3-butanedione and 2-butanone at 1 and 10 atm, the azeotrope moves from 2-butanone mole composition of 0.88 at 1 atm to 0.67 at 10 atm. It is suitable for this mixture to study the PSD system.

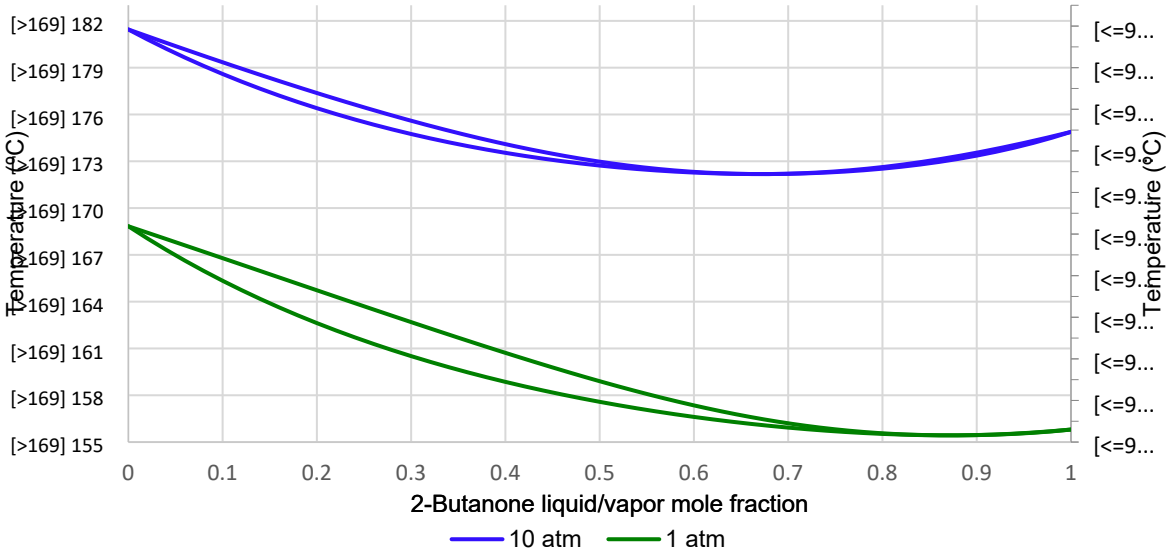

Figure 2: Binary diagram of 2-butanone and 2,3-butanedione at 1 and 10 atm

The proposed separation procedure of the ternary mixture (schematized in Figure 3) is the following: first, pure cyclopentanone is obtained in the bottoms of the first distillation column, operating at atmospheric pressure. The distillate, a mixture of 2-butanone and 2,3-butanedione is conducted to a second column, operating at ambient pressure too, and getting as a residue 2,3-Butanedione, and as distillate a mixture of 2,3-butanedione and 2-butanone on its azeotropic composition at 1 atm. This stream is pressurised and introduced to a third column, where pure 2-butanone is collected at the bottoms, and a mixture of 2,3-butanedione and 2-butanone on its azeotropic composition at high pressure is obtained as distillate, which is recirculated to the second column.

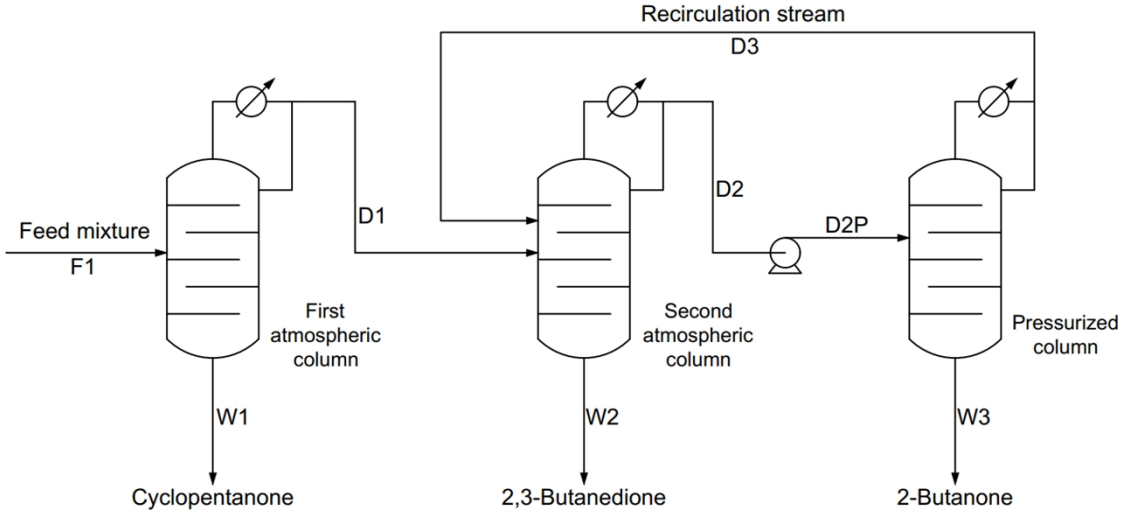

Figure 3: Proposed flowsheet for the separation process

The methodology used is the following: first, random values for the design variables are generated through MATLAB ® (in this case, twenty sets of values, which is known as the first generation), and these are sent to Aspen ®, where rigorous simulations are performed. Once the simulations are converged, the outputs are sent to MATLAB ®, which evaluates the results and creates a new generation. In each generation, the objective

function determines the suitability of each solution and depending on these values, some of them are selected to be a parent for the next generation. The procedure is then more likely to select the best solutions for the next generations, eliminating the worst ones.

2.2 Design specifications and simulation

The study of Shang et al. (2022) has been taken as reference for fixing the design specifications, feed conditions are summarized in Table 1.

Table 1: Feed specifications

Feed operating conditions	Value
Temperature (K) (boiling point)	361.3
Molar flow rate (kmol/h)	100.00
Molar fraction Cyclopentanone	0.200
Molar fraction 2,3-Butanedione	0.400
Molar fraction 2-Butanone	0.400

The purity of the products is set to 0.99 molar fraction for cyclopentanone and 2-butanone, while product 2,3-butanedione flow is 39.80 kmol/h.
The twelve variables to be optimised (design variables) are the number of stages in column 1 (first atmospheric column), number of stages in column 2 (second atmospheric column), number of stages in column 3 (pressurized column), feed stage of fresh feed in column 1, feed stage of stream from column 1 to column 2, feed stage of stream from column 3 to column 2 (recirculation stream), feed stage of stream from column 2 to column 3, pressure of column 3 (pressurized column), reflux ratio in column 1, reflux ratio in column 2, reflux ratio in column 3, and recirculation stream flow.

3. Results and discussion

3.1 Genetic algorithm

Several tests have been done in order to achieve a good combination of the parameters of the genetic algorithm such as the population size or the crossover and mutation ratio. In the end, the best results are shown in Table 2, where crossover and mutation ratio are related to how the generations are obtained. In the crossover operation, two individuals are chosen from the previous generations (known as parents) and their chains of variables are crosslinked, while the mutation operation refers to swapping a certain gen of the parent.

Table 2: Genetic algorithm input parameters

Input parameters	Value
Generations	100
Population	20
Number of elite individuals	1
Crossover ratio (%)	50
Mutation ratio (%)	50

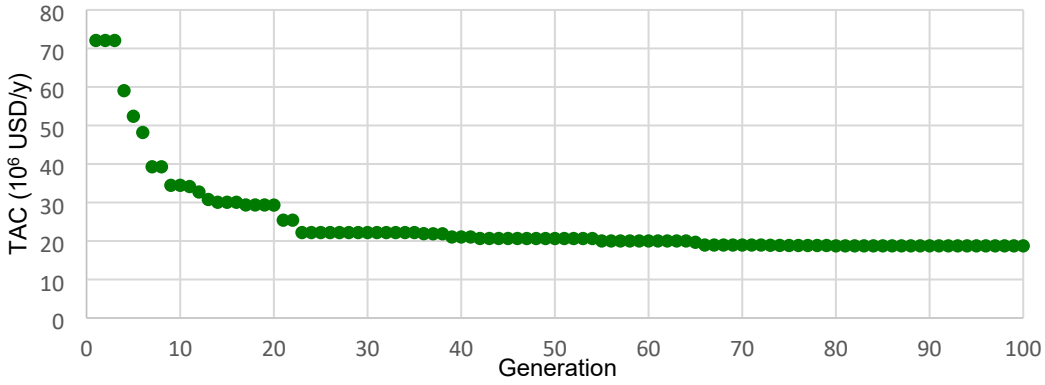

Figure 4: Evolution of the objective function through the generations

The results of the genetic algorithm show that the TAC improves 74 % between the first and last generation, with a computational time of 100 min, for a CPU: Intel Core I i5-3330 CPU @ 3.00GHz 3.20 GHz; RAM: 8 GB. In Figure 4, the evolution of the objective function through the generations is represented. In the first generation, the objective function improves quickly, this is due to the fact that it is easy for the algorithm to find better points. From generation 10 onwards, the function continues to improve but at a slower rate. Finally, from generation 65 onwards the algorithm is not able to find better points (or this improvement is very small), so there is a flatness in the graph.

3.2 Rigorous simulation

The values for the optimised variables are presented in Table 3.

Table 3: Comparison of the results of this work versus Shang et al. (2022)

	This work			Shang et al. (2022)	
Number of columns	3			2	
Column number	1	2	3	1	2
Number of stages	20	40	44	66	24
Feed stages	9	32/29	27	28	11
Reflux ratio	0.5	15	14.6	15.22	3.25
Pressure (atm)	1	1	18.4	1.58	1.97
Reboiler duty (kW)	1114	8983	2691	-	-
Condenser duty (kW)	1109	9138	2265	-	-
Recirculation stream flow (kmol/h)	24.03			No recirculation	
TAC (10^6 USD/y)	18.733			-	

Comparing Shang et al. (2022) and the process scheme proposed in this work, the main difference is that Shang et al. (2022) uses two columns instead of three. This two-column system has been simulated in Aspen Plus ®, but the complete separation has not been achieved due to the impossibility of breaking the azeotrope at the given pressures (between 1.58 and 1.97 atm). Values of reflux ratios of columns 2 and 3 (15 and 14.6) contrast with column 1 (0.5), this could be due to the 2-butanone and 2,3-butanedione binary diagram, whose curves are overlapped on the right side of the azeotrope (see Figure 2). In consequence, the separation of the binary mixture becomes harder. Pressure of the high-pressure column is 18.4 atm, higher than what is usually taken in the literature about pressure-swing distillation. According to Risco et al. (2019), around 70 % of the literature fixes the pressure of the high-pressure column, parameter that has been set as a design variable in this work. It can also be seen that most of the energy of the process (around 70 %) is used in the second column. With all these considerations, the TAC value for 100 kmol/h of fresh feed is $18.7 \cdot 10^6$ USD/y.

The results of the major streams of the simulation are collected in Table 4, where stream names correspond to the names in Figure 3: fresh feed (F1) enters the first column at ambient pressure and compositions according to the design specifications (above-mentioned in Table 1). Cyclopentanone is collected in the residue (W1), while the distillate (D1) has molar composition of 0.5 of 2.3-butanedione and 0.5 of 2-butanone. This equimolar mixture is conducted to the second atmospheric column, along with the recirculation stream (D3), obtaining a residue (W2) of purified 2,3-butanedione and a distillate (D2) with a composition corresponding to the azeotrope composition at 1 atm, which is pressurized (stream D2P) and fed to the pressurized column, obtaining a residue (W3) of purified 2-butanone, and the distillate (D3) at the corresponding azeotropic composition at 18.4 atm, which is recirculated and fed to the second column along with the distillate stream (D1).

Table 4: Results of the major streams of the simulation

Item / Stream	F1	W1	D1	W2	D2	D2P	W3	D3
Temperature (ºC)	88.2	130.0	80.5	88.8	78.9	81.3	208.8	205.0
Pressure (atm)	1.0	1.0	1.0	1.0	1.0	18.4	18.4	18.4
Molar flow rate (kmol/h)	100.00	20.02	79.98	39.80	64.35	64.35	40.18	24.17
Molar fractions								
Cyclopentanone	0.200	0.999	traces	traces	traces	traces	traces	traces
2,3-butanedione	0.400	0.001	0.500	0.994	0.136	0.136	0.010	0.346
2-butanone	0.400	traces	0.500	0.006	0.864	0.864	0.990	0.654

Regarding the results of the major streams, it is important to note that cyclopentanone is almost completely separated from the system in the first column (stream W1), as there are no azeotropes involving this compound and its separation is simpler. The composition of W2 (0.994), is fixed from the design specifications due to the mass balances.

4. Conclusions

A novel three-columns separation process for the mixture of cyclopentanone, 2,3-butanedione and 2-butanone has been designed and optimised. Genetic algorithms have been successfully applied to optimise this process. Linking MATLAB ® and Aspen Plus ® provides a way to separately carry out the optimisation procedure and the simulation process, improving the task of finding the optimal solution. A pressure-swing distillation system has been applied to break the azeotrope. This process has not been studied before for this mixture. Among the main results, the global heating services are 12,788 kW and cooling services are 12,512 kW. Final TAC value for processing 100 kmol/h of crude feed is $18.7 \cdot 10^6$ USD/y. Petrochemical processes have been studied for years and they are highly optimised. However, pyrolysis of biomass is a newer process and the separation of its components needs to be optimised to become more efficient and competitive.

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