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Process design for the recovery of valuable organic compounds from pyrolysis oil aqueous phase

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ABSTRACT

Pyrolysis, a key waste-to-X technology, enables converting a wide portfolio of biomass waste into valuable chemicals and fuels. However, raw pyrolysis oils are chemically and physically unstable. A multi-step stabilisation is necessary to reduce acidity and the content of reactive components, mainly carbonyls and carboxylic acids. During stabilisation, which involves deoxygenation and hydrogenation as the main steps, an aqueous phase is generated as a by-product. This stream contains mainly water, but relevant amounts of methanol and ethanol (2-8 wt%) are also present, together with minor concentrations of higher alcohols, C_1-C_4 carboxylic acids, and light esters. The aim of this work is to design and optimise a process to isolate the methanol and ethanol embodied in the aqueous phase and exploit them as intermediates to generate biofuels, biochemicals, and pharmaceutical products. The process consists of a train of four distillation columns to maximise the recovery rate and purity of the two targeted products. COCO-COFE, a CAPE-OPEN process simulator, is used for flowsheet development. The optimal number of theoretical stages and the optimal positioning of the feed to each unit have been optimised, considering a trade-off CAPEX-OPEX as the criterion. Results show that up to 95% and 98% yield can be achieved for methanol and ethanol, respectively. Methanol purity is limited to a maximum of 92 wt% due to the presence of volatile impurities, while ethanol contains residual propanol (6 wt%). The overall heat demand is in the order of 1 MJ/kg feed.

Keywords: waste valorisation, process design and modelling, process optimisation, organics recovery from wastewater, multistep distillation

INTRODUCTION

Fast pyrolysis is considered a high-potential route to produce sustainable advanced biofuels. However, Fast Pyrolysis Bio Oil (FPBO) is not suitable for direct use as a transportation fuel, and further chemical upgrading is required to enhance stability. Different approaches can be adopted to reduce the concentration of acidic compounds, including co-processing in Fluid Catalytic Cracking (FCC), and hydrotreating. The Biomass Technology Group (BTG), a private Dutch company specialised in converting biomass into sustainable biofuels, has developed a proprietary stabilisation process using a Ni-Cu-based catalyst called Picula™ [1]. This process, which is shown in Figure 1, includes the following main steps [2]:

1. Selective hydrogenation at mild temperatures (200-250°C). The obtained product is called Stabilised Pyrolysis Oil (SPO);
2. Deoxygenation at high temperature (350°C). The obtained product is called Stabilised Deoxygenated Pyrolysis Oil (SDPO);
3. Final hydrogenation (refinement step at 425°C) to produce Hydrogenated Pyrolysis Oil (HPO).

This FPBO stabilisation process generates a liquid product that comprises both an organic and an aqueous phase. The presence of a water phase is largely determined by the substantial water content present in the biomass feedstock. Aqueous phase from pyrolysis is a complex mixture of water (> 60 wt%) and various dissolved organic compounds, including alcohols (methanol, ethanol, propanol, and butanol), sugars (levoglucosan and others), carboxylic acids (mainly acetic, propionic,

and butyric acid), esters, furfural, guaiacol, and minor quantities of aldehydes and ketones. The aqueous phase is generally disposed of as waste or potentially utilised as co-feed in biogas plants. However, given its composition, it could be considered a valuable resource for producing various bio-based chemicals and fuels, though the chemicals of interest are extremely diluted in water. Therefore, up-concentration and purification are needed, which makes the process economically challenging. The aim of this work, which is carried out within the framework of the FUEL-UP project [3] funded by the European Commission, is to design and optimise a process to isolate the chemicals embodied in the aqueous phase.

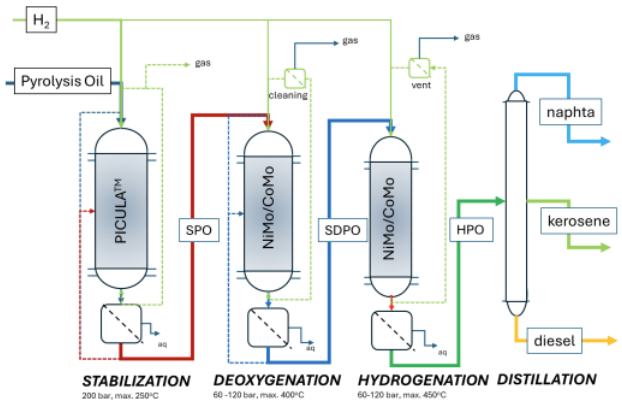

Figure 1. The FPBO upgrading process developed by BTG [2].

The idea is to separate aqueous/organic phase and subsequently treat the two phases individually [1]. The water phase can be further processed to separate and recover valuable chemicals. However, water-alcohols-carboxylic acid mixtures have an azeotropic nature, which makes compounds separation challenging.

One viable option is extractive distillation. This approach can effectively isolate polar components, such as alcohol and acetic acid, enabling their direct use as valuable products or in subsequent processes like biofuel upgrading [4]. Alternatively, azeotropic distillation can be used to remove water from the aqueous phase of pyrolysis oil by utilising the formation of azeotropic mixtures [5]. However, these technologies suffer from the introduction of a third component (the entrainer) during the separation process as a major drawback [4]. This can lead to relevant final product purity issues. Besides, the plant layout complexity considerably increases, and there is a need for heat integration to minimise the energy consumption of product recovery and solvent regeneration. Recently, other advanced separation options have also been investigated, including freeze concentration, reverse osmosis, or bioconversion. However, these technologies are all characterised by a much lower Technology Readiness Level (TRL).

For these reasons, in this work, a train of distillation columns in series is identified as the simplest and most robust separation scheme:

- The first distillation column allows a bulk removal of C_1-C_3 alcohols and eventual other species whose boiling point is lower than water;
- A variable number of downstream columns can be used to refine the separation.

FEEDSTOCK CHARACTERISATION

The composition of the water phase obtained during Stabilised Pyrolysis Oil (SPO) and Stabilised Deoxygenated Pyrolysis Oil (SDPO) production at BTG has been measured using GC-FID (Gas Chromatography - Flame Ionization Detector) technique in SINTEF, and it is shown in Table 1. 14 different species were identified, and their concentration was quantified through calibration curves. The remaining peaks of unidentified species were combined with the peaks of the nearest species observed in the chromatogram (closest retention time).

Table 1: Composition of the aqueous phase samples from SPO (SPO_{Aq}) and SDPO ($SDPO_{Aq}$) measured with GC-FID. Acronyms: water (H2O), methanol (MeOH), ethanol (EtOH), 1-propanol (1-PrOH), 1-butanol (BuOH), acetic acid (AcAc), tetrahydrofuran (THF), Methyl acetate (MeA), ethyl acetate 8EtA), acetone (Acet), formic acid (FoAc), isopropanol (2-PrOH), propionic acid (PrAc), butyric acid (BuAc), 1-pentanol (PeOH).

	GC-FID results		For simulation	
Component	**SPO_{Aq}**	**$SDPO_{Aq}$**	**SPO_{Aq}**	**$SDPO_{Aq}$**
H2O	72.50	89.90	85.60	94.22
MeOH	4.95	0.33	5.84	0.35
Ethanol	2.70	1.85	3.19	1.94
1-Propanol	0.32	0.55	0.38	0.58
Butanol	0.13	0.03	0.15	0.03
Acetic Acid	0.22	0.00	0.26	0.00
THF	0.23	0.19	0.27	0.20
Methyl Acetate	0.25	0.00	0.30	0.00
Ethyl Acetate	0.59	0.49	0.70	0.51
Acetone	0.05	0.08	0.06	0.08
Formic Acid	0.05	0.05	0.06	0.05
Isopropanol	0.20	0.10	0.24	0.10
Propionic Acid	0.23	0.47	0.27	0.49
Butyric Acid	0.37	0.50	0.44	0.52
Pentanol	1.91	0.87	2.26	0.91
SUM	84.70	95.41	100.00	100.00

For simplicity, alcohols heavier than C_5

(concentration below 0.1 wt%) were lumped into pentanol, and carboxylic acids higher than C_4 were lumped into butyric acid. The concentrations of the compounds detected with the GC cover 85% and 95% of the mass balance for SPO_{Aq} and $SDPO_{Aq}$, respectively. For modelling purposes, the composition has been normalised to 100%, as shown in Table 1.

PROCESS DESIGN

Thermodynamic model

In water-alcohols-carboxylic acids systems, strong non-idealities are present due to the azeotropic nature of most of the involved binary interactions. Activity models like Non-Random Two-Liquids (NRTL) and UNIQUAC are the most suitable to describe VLE of this system. However, it has been verified that the existing default NRTL models available in Aspen Plus and COCO-COFE V3.7, a license-free software released by AmsterChem, do not accurately reproduce the equilibrium measurements of most of the binary and ternary mixtures involving the 14 compounds of interest for this application. Therefore, the NRTL model has been re-parametrised to increase predictability. The NIST ThermoData Engine V10.3 was used as the experimental data source. The re-fitted model shows a significantly improved capability to reproduce experimental data, as the Average Relative Deviation (ARD) in the prediction of vapor phase composition at fixed liquid composition and temperature (for isothermal data) or pressure (for isobaric data) drops from 16% and 12.1% of the current COFE and Aspen models, respectively, down to 7%.

Details on the procedure followed for the mode reparametrisation and the outcomes of its performance evaluation are described in a separate contribution.

Process Flow Diagram

The Block Flow Diagram of the designed process for efficient recovery of methanol and ethanol at the highest possible purity is drawn in Figure 2. It consists of a train of four distillation columns in series:

- The first column (Col. 1) is a bulk water removal;
- The second column (Col. 2) separates methanol from ethanol;
- The third column (Col. 3) is a methanol purification step. The target is to minimise the residual concentration of acetone, acetates, and THF. Given the azeotropic nature of most mixtures including the mentioned compounds, there is a limit in the maximum amount of impurities that can be removed by simple distillation. Two scenarios have been investigated: scenario A has maximum methanol purity as the target, while in scenario B methanol recovery is maximised.
- The last column (Col. 4) is an ethanol purification step. The target is to minimise the residual concentration of water and heavier alcohols, with a special focus on propanol.

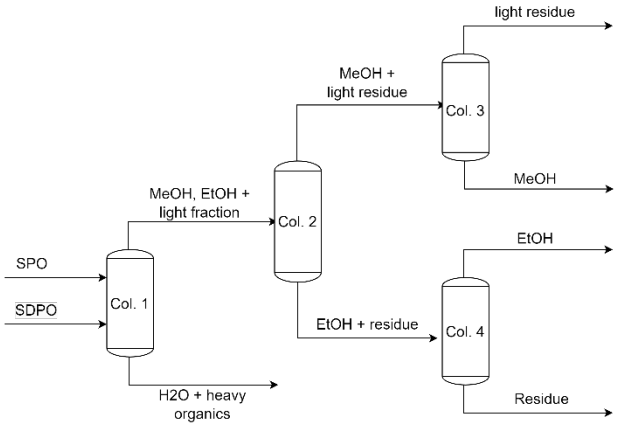

Figure 2. BFD of the distillation process designed for methanol and ethanol recovery from pyrolysis oil stabilisation wastewater.

Three case studies are analysed considering three different feedstocks:

- Only SPO_{Aq} stream (CS1);
- Only $SDPO_{Aq}$ stream (CS2);
- Combined SPO_{Aq} + $SDPO_{Aq}$ streams (CS3).

The same process layout and the same specifications are used to run each case study. A small variation is introduced when $SDPO_{Aq}$ only is treated: given its very low methanol content, column 3 is removed in this configuration.

The specifications set to design each distillation column are gathered in Table 2.

Table 2: List of the specifications chosen to model each distillation column.

Column	Top / bottom	Specification	Value
Column 1	Top	EtOH recovery	99%
	Bottom	H2O recovery	99%
Column 2	Top	MeOH recovery	99.99%
	Bottom	EtOH recovery	99.99%
Column 3, scenario A	Top	THF recovery	95%
	Bottom	EtA recovery	20%
Column 3, scenario B	Top	THF recovery	55%
	Bottom	MeOH recovery	95%
Column 4	Top	EtOH recovery	99%
	Bottom	1-PrOH recovery	95%

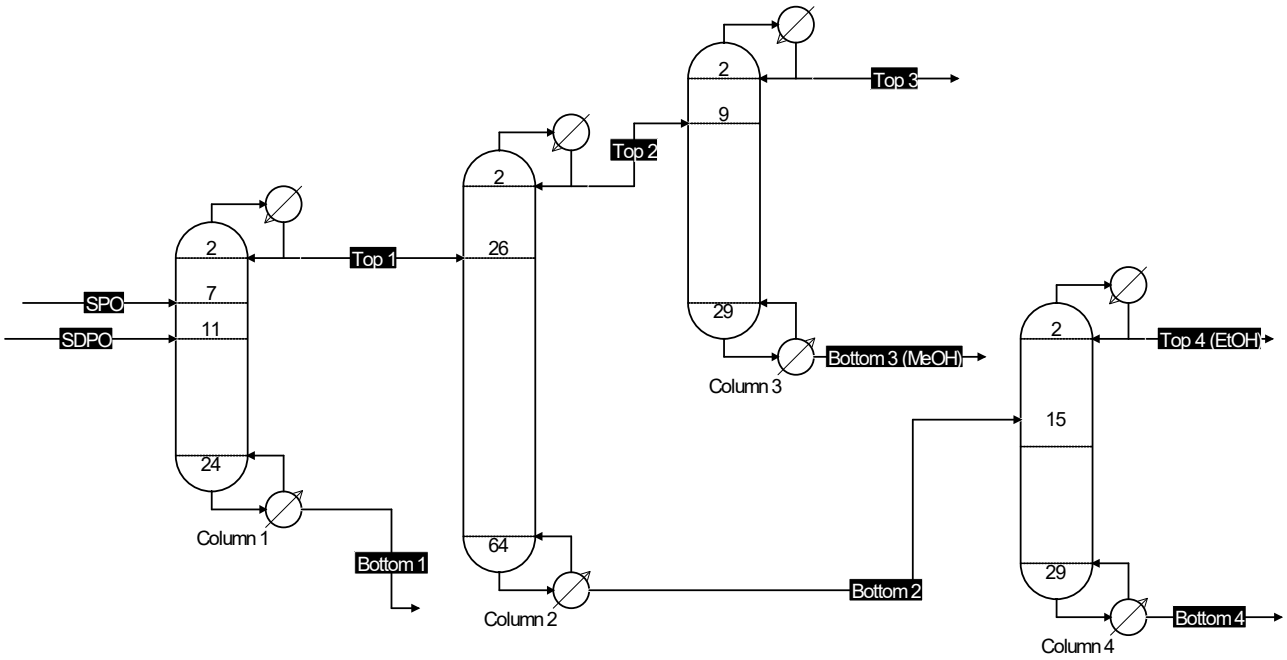

Figure 2. Process flowsheet implemented in COCO-COFE process simulator for methanol and ethanol recovery from combined SPO_{Aq} and $SDPO_{Aq}$ streams.

Process optimisation

The optimal number of theoretical stages and the optimal positioning of the feed to each column are optimised, considering a trade-off CAPEX-OPEX as the criterion. Indeed, increasing the number of theoretical stages results in a decrease in the energy demand for the separation, but it also generates an increase in the investment costs to build the column. More specifically, the minimum number of stages for which an increment lower than 5% is observed in the reboiler duty compared to a configuration with 5 additional stages is selected as the optimum. Noteworthily, only the reboiler duty is considered for the optimisation, while the cooling energy demand for the condenser is neglected. This choice can be justified based on the utilities needed in the reboiler and condenser. Indeed, the operating temperatures in each of the four columns are such that low-pressure steam is required as the utility in the reboiler, while standard cooling water can be used for distillate condensation.

As for the feed positioning, feeding from the top to the bottom of the column is investigated (with a step of two stages), and the feed position associated with the lowest reboiler duty is chosen as the optimum.

Flowsheet implementation

The Block Flow Diagram (BFD) shown in Figure 2 is used as the basis to develop a process flowsheet. The simulation is implemented in COCO-COFE, a license-free and CAPE-OPEN flowsheet environment released by Amsterchem. A size of 3 ton/h of SPO_{Aq} and 3 ton/h of $SDPO_{Aq}$ feed is assumed as representative of a commercial-scale application of the proposed technology.

A screenshot from the simulation developed for the combined SPO_{Aq} and $SDPO_{Aq}$ feed is drawn in Figure 2.

RESULTS

Optimal column sizing

The optimal theoretical stage number and the optimal feed positioning identified for each column are gathered in Table 3. These are the same for all three case studies.

Table 3: Results of distillation column layout optimisation.

Column	Optimal N stages	Optimal feed stage
Col. 1	25	7, 11
Col. 2	65	26
Col. 3, scenario A	20	2
Col. 3 scenario B	35	25
Col. 4	35	22

Product recovery rate and purity

The yield and purity of methanol and ethanol obtained from the optimised process model are gathered in Table 4.

Table 4: Methanol and ethanol yield (%) and purity (wt%) obtained in the different modelled process configurations. Components' acronyms are retrieved from Table 1.

Comp.	Scen.	KPI	CS1	CS2	CS3
MeOH	A	Yield	56.0	-	51.0
MeOH	A	Purity	95.5	-	92.2
MeOH	B	Yield	94.6	-	94.9
MeOH	B	Purity	88.1	-	81.1
EtOH	-	Yield	98.0	93.1	98.0
EtOH	-	Purity	85.5	85.7	86.0

Results indicate that there is a trade-off between methanol yield and purity. Indeed, a high recovery rate can be achieved (95%, scenario B), but the corresponding product quality is relatively poor (81-88 wt%). On the other hand, increasing the methanol purity up to 95 wt% is possible (scenario A), but in this case, only 56% of the total methanol content present in the feed is recovered in the final product stream. The reason behind this observation is that the presence of volatile impurities negatively affects the product quality, as these compounds have boiling points close to methanol, and some of them form non-ideal interactions, which makes their separation via distillation more challenging. The detailed composition of the methanol product stream obtained when using SPO_{Aq} only, or combined SPO_{Aq} and $SDPO_{Aq}$ feed, is reported in Table 5.

Table 5: Methanol composition (wt%) in the different modelled process configurations. Components' acronyms are retrieved from Table 1.

Component	CS1	CS1	CS3	CS3
Scenario	A	B	A	B
MeOH	95.50	88.14	92.20	81.06
EtA	4.08	8.94	7.11	15.88
THF	0.40	2.36	0.67	2.85
Acet	-	0.32	-	0.17

The most abundant impurity is ethyl acetate, which is predicted to reach concentrations above 7 wt% in the combined feed case study. Indeed, the re-parametrised NRTL model used in this work indicates that methanol (MeOH) and ethyl acetate (EtA) form a minimum-boiling azeotrope at a methanol concentration of 70 vol% (see Figure 3), and the bubble and dew curves become flat and close for higher methanol concentrations, which indicates that the mixture is difficult to separate by conventional distillation methods. Notably, MeOH-EtA VLE represents the most constraining azeotropic behaviour on the methanol product purity, and this observation holds for all the analysed case studies.

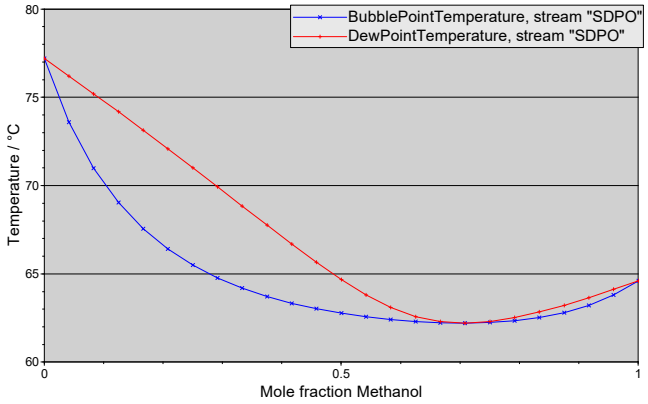

Figure 3. Temperature-composition VLE diagram for the binary mixture MeOH-EtA obtained with the re-fitted NRTL model.

Ethanol is obtained at a purity ranging between 85 wt% and 86 wt%. It contains residual water and C_3 alcohols, mainly isopropanol. Indeed, isopropanol forms an azeotrope with a comparable composition and boiling point of the water-ethanol one, which hinders their separation. The detailed ethanol product stream composition is gathered in Table 6.

Table 6: Ethanol composition (wt%) in the different modelled process configurations. Components' acronyms are retrieved from Table 1.

Component	CS1	CS2	CS3
EtOH	85.49	85.74	85.98
H2O	7.93	7.88	7.94
2-PrOH	6.28	4.90	5.68
1-PrOH	0.28	0.66	0.39
MeOH	-	0.81	-

The highest methanol purity is achieved in CS1. Given that a substantial amount of residual volatile organics is present in the final product, maximising yield (scenario B) looks the most promising option. On the other hand, ethanol yield and purity prove to be not affected by the type of feedstock, with comparable results achieved in all the investigated case studies.

Energy requirements

The total thermal energy demand of the process is calculated as the sum of the reboiler duties of all four columns (three for CS2), and the results are shown in Table 7. As the bottom temperature ranges from 63°C to 99°C in all columns, low-pressure steam is the required utility.

CS2 is the option associated with the lowest energy demand, but in this case only ethanol is recovered as a product. Recovering methanol and ethanol from both SPO and SDPO aqueous streams in the same plant (CS3) is more energy efficient than treating the SPO aqueous stream only. The total duty is around 1 MJ/kg of treated

aqueous stream, resulting in a 16% reduction in the heat demand.

Table 7: Specific energy requirement (in MJ/kg feed) of the distillation process for methanol and ethanol recovery.

Case study	Scenario A	Scenario B
CS1	1.16	1.15
CS2	0.73	0.73
CS3	0.95	0.97

CONCLUSIONS

A distillation-based process for the recovery of valuable organic compounds, namely alcohols, from pyrolysis oil wastewater stream has been designed, modelled, and optimised. This study shows that there is potential for ethanol and methanol recovery for applications in fuel blending. These alcohols can be effectively separated from water and other heavier compounds: high recovery rates (> 95%) can be achieved by adopting a simple process layout made up of four distillation columns in series, which minimises investment costs. Moreover, no third compound is introduced to avoid contamination effects.

However, the presence of detectable concentrations of esters (i.e., methyl acetate and ethyl acetate), and furans (like tetrahydrofuran) together with alcohols in the SPO and SDPO-derived aqueous mixtures represents a major challenge since all these species have a similar boiling point range as methanol and ethanol. As a result, the obtained alcohol purity is limited.

To target applications requiring a higher degree of purity, such as in the chemical industry, the separation scheme becomes more complex, and an unspecified number of additional purification steps/columns need to be added in a future process layout.

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