

Simulation of eucalyptus bio-oil and Brazilian crude oils blends distillation: effects, challenges and opportunities.

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Abstract. Potentially obtained from different sources, in particular from agro-industrial feedstocks such as sugarcane, soybean and eucalyptus - all abundant in Brazil - the complex, acidic and unstable fast pyrolysis bio-oil mixture of components presents opportunities and challenges to compose production routes of renewable fuels and chemicals. So far, most of coprocessing efforts were towards its blending with VGO in FCC, which presented good products quality and satisfactory renewable carbon captured in liquid output. An unexplored approach was presented in this work, focusing on coprocessing in atmospheric and vacuum distillations using Aspen Plus® V11 simulations. An average of 10.3 wt.% of biogenic compounds was achieved in naphtha, kerosene and diesel fractions, favored by 20 - 25 °API crude oils blending. Desalting unit is the major bottleneck to co-distillation with 40 - 50 wt.% renewable content separated in aqueous waste stream, followed by average energy input increase from 78 to 703 GJ.bbl⁻¹.

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1. Introduction

Between 2011 and 2020, biofuels production around the globe increased from approximately 108 to 151 Mm³ (36%)¹. Brazil contributes to this increase with an increase of approximately 53.5% (25.6 to 39.2 Mm³) and presents clear growth trend for the sector in the next decade². In general, renewables have been used as standalone fuels or in blends with fossil correspondents (e.g., E100 and E27), strategy referred by the National Advanced Biofuels Consortium (NABC) (USA) as coprocessing by insertion point 3 or finished products blending. Differently, insertion points 1 and 2 corresponds to the blending of renewable fluids with non-finished products, in earlier stages of crude oil and intermediates fractions processing, respectively, which is commonly referred as coprocessing³.

Coprocessing with intermediates has been investigated focusing mainly in two different methods. The first is blending of hydrogenated vegetable oil (HVO) into fossil diesel range petroleum fractions, which is still under development and tests due regarding quality standards.

The second route is the fast pyrolysis or hydrothermal liquefaction products blending with gas oils. Hydrothermal liquefaction (HTL) decomposes biomass to 250 – 300 °C and 100 – 150 bar in the presence of solvents such as water or ethanol. Apart from producing a considerably more stable fluid than the fast pyrolysis process, HTL is costly due to the severe conditions, therefore slowing down development of the topic, which still remains on pilot scale.⁴

Differently, fast pyrolysis process is less severe (1 to 5 bar, 350 to 500 °C, inert atmosphere)^{5,6} and more profitable (considering technological maturity)^{3,7}, already applied in commercial scales to produce bio-oil⁸, biochar and syngas⁶, the two last products usually destined to heat integration in circulating fluid-beds and CHP cycles^{9,10}.

Fast pyrolysis bio-oil (FPBO) is acidic, unstable, mixture of chemically diverse hydrocarbons generated from the thermochemical decomposition of biomass⁶. The depolymerization, dehydration and decarboxylation reactions generate highly oxygenated acids, aldehydes, phenols, sugars and oligomers, composing a multi-phase emulsion that destabilizes in exposure to air and mild temperatures¹¹. An upper layer is an organic, acidic phase, rich in lower molecular weight extractives. Middle layer is composed by an aqueous phase, with high solubility of sugars and light oxygenated compounds. Lastly, the bottom, viscous organic layer is rich in lignin derived components and phenolics.¹² This multiphase behavior varies subject to many compositional parameters, such as ash and water contents, as well as operational parameters such as the method of bio-oil condensation.¹¹

FPBO composition is highly dependent on feedstock used and pyrolysis process conditions.¹³ Wood-produced bio-oils present yield inversely dependent both to biomass particle size and catalytic reactions, this last parameter responsible for generating higher amounts of water in liquid product.^{5,14} Moreover, several studies reported higher contents of carboxylic acids, furans and ketones in forestry feedstock bio-oils (specially eucalyptus), while agriculture biomass tend to generate bio-oil with more phenolic groups.¹⁵ The chemical structure influence was also observed in bio-oil yield, being reported a higher bio-oil formation in hardwood (e.g., eucalyptus) than softwood (e.g., pine) most likely due to lower activation energy of wood structure in pyrolysis reactions.^{16,17}

In Brazil, with climate, land extension and technological advantages^{18,19,20}, there are several potential feedstocks for biofuels or intermediates production. Along with sugarcane and soybean, already extensively used for bioethanol and biodiesel production, respectively, softwood and hardwood are abundant for cellulose and wood production and potential candidates for bio-oil feedstock.^{21,22,23,24}

Identifying this potential, a promising route was explored by Petrobras, coprocessing pine wood FPBO with vacuum gasoils (VGO) in a Petrobras (Brazil) demonstration-scale FCC unit. The experiment exposed a clear possibility of renewable fractions produced for gasoline and diesel, with minor quality impacts up to 10% input renewable content. However, improvements are being developed, as the same group also traced renewable carbon throughout the experiment, acknowledging that only 30 to 40 wt.% was present in the finished liquid product.^{8,25,26}

Opposingly, insertion point 1 (distillation) has almost not been explored in literature, neither theoretically or experimentally, with only few studies showing low distillation temperatures and vaporized yields (e.g., < 40 wt.%), percentage slightly increased up to 67 wt.% with molecular distillation and up to 72 wt.% with hybrid, mathematical-empirical models for bio-oils in general.^{27,28,29,30} This percentage was also achieved with wood biomass (pine and cedar) bio-oils distillation experiments, limitation that correlates to polymerization of sugars and lignin oligomers, increasing boiling point and viscosity significantly.^{31,32,33}

Apart from distillation, FPBO is not miscible in crude oils, separating phases in lower °API crudes and creating emulsions in heavier crudes at low blending ratios, which is reported to potentially improve processability by lowering viscosity.^{34,35,36,37} Due to this challenge, surrogate-composition of bio-oil is often used in simulations, as a fairly precise method of representing fluid's properties.^{23,38,39,40,41,42,43,44,45,46,47} These simulations, however, are focused only on wood pyrolysis and further bio-oil upgrading, without distillation detailing. Also, no coprocessing simulations of crude oil and bio-oil are reported.^{42,48,49,50,51,52,53,54}

Therefore, the aim of this study is to close this simulation gap, coprocessing distillation of surrogate eucalyptus bio-oil components with selected Brazilian crude oils, including desalting, atmospheric distillation and vacuum distillation units. Besides mass and energy balances, this work also focuses in distilled fractions' properties and renewable content recovered.

2. Materials and Methods

2.1. Surrogate eucalyptus fast pyrolysis bio-oil (FPBO)

Surrogate composition of eucalyptus bio-oil was defined investigating chromatographic analysis from several different studies.^{39,56,57,58,59,60,61,62,63}, as well as chemical decomposition routes for heavy components screening.^{65,66,67,68,69}

Multi-objective optimization of molar ratios was performed ($1.35 < H/C < 1.50$ and $0.35 < O/C < 0.45$) using the average groups fractions reported and varying heavy lignin derived components ($5 < \text{wt}\% < 20$), water ($18 < \text{wt}\% < 25$) and sugars ($5 < \text{wt}\% < 18$) constraints. Also, the contribution of each component in bio-oil was defined by average molecular weight and boiling point.⁶

A mixture of 40 components divided into 13 chemical groups were selected. The groups defined were: acids (7.67 wt.%), alcohols (1.06 wt.%), aldehydes (1.02 wt.%), aromatics/furans (2.60 wt.%), ethers (1.57 wt.%), esters (1.72 wt.%), nitrogenated (0.49 wt.%), hydrocarbons (1.58 wt.%), ketones (4.24 wt.%), phenolics (17.52 wt.%), sugars (18.00 wt.%), lignin derived heavy components (18.12 wt.%) and water (24.40 wt.%).

By wt% in group the components defined were: acids: acetic acid (73.98%), 4-hydroxy-3-methoxy-benzoic acid (8.55%), propanoic acid (17.47%); alcohols: 2-furanmethanol (24.87%), methanol (44.87%), 3-buten-2-ol (30.26%); aldehydes: furfural (8.40%), formaldehyde (10.72%), glutaraldehyde (80.87%); aromatics/furans: furan (17.69%), 2,3-dihydrobenzofuran (37.86%), 1,2,4-trimethoxybenzene (44.45%); ethers: eucalyptol (100%); esters: 1,2-dimethyl-propyl acetate (40.06%), octyl acetate (59.94%); nitrogenated: 2,4,6-trimethylpyridine (73.68%), dibenzopyrrole (26.32%); hydrocarbons: 4-ethenyl-1,4-dimethylcyclohexene (50%), 1-ethyl-1-methyl-cyclopentane (50%); ketones: 2-(3H)-dihydrofuranone (11.85%), 3-hydroxy-2-methyl-4H-4-pyranone (35.33%), 3-methyl-1,2-cyclopentanedione (46.57%), 1-hydroxy-2-propanone (6.25%); phenolics: 2-hydroxyphenol (30.37%), 2-methoxy-4-(prop-1-en-1-yl)phenol (16.59%), 4-hydroxyphenol (11.23%), 2,6-dimethoxyphenol (17.12%), phenol (24.70%); sugars: levoglucosan (21.02%), β -D-arabinopyranose (54.67%), cellobiose (24.31%); lignin der.: 2,6-dimethoxy-4-(3-hydroxyprop-1-enyl)phenol (12.5%), 2-methoxy-4-(3-hydroxy-1-propenyl)phenol (12.4%), 4-(3-hydroxy-1-propenyl)phenol (12.5%), 3,5-dimethoxystibene (12.52%), dehydroabietic acid (12.53%), dibenzofuran (12.53%), pinoresinol (12.51%), 2-phenyl-2,3-dihydro-1-benzofuran (12.52%).

The mixture, was inserted in Aspen Plus® for properties calculations. Each component chemical structure and UNIFAC contribution groups were inserted manually, for missing properties estimation through Aspen's property constant estimation system (PCES). Pinoresinol and 2-phenyl-2,3-dihydro-1-benzofuran were inserted as pseudocomponents, chemical structure, molecular weight and boiling point as required inputs.⁶¹ In the same way, any other component with missing chemical structure, UNIFAC groups or property correlations, was manually adjusted by user, with help of NIST database access by Aspen Plus®.

2.2. Brazilian crude oils

Three different crudes were investigated in three conditions (0, 5 and 10% renewable blend). These scenarios used specifically selected light, medium and heavy crude oils as main blends' constituents: Iracema field (2016) (32.6 °API), Lapa field (2011) (22.8 °API) and Peregrino field (2016) (13.2 °API), respectively. The blends were labeled with "L", "M" or "H", plus the percentage of the crude present, plus "R" followed by the percentage of renewable content (e.g., L095R005; Light crude 95vol%, Bio-oil 5vol%).

Lapa field data was retrieved from Total Energies Assay Database (publicly available), the company is the field operator (45%), together with Shell Brasil Petróleo (30%) and Repsol Sinopec Brasil (25%). Iracema field data was retrieved from Aspen Hysys® Assay Database and is operated by Petrobras (65%), Shell Brasil Petróleo (25%) and Galp Energia (10%). Peregrino field data was retrieved from Equinor Assay Database (publicly available), the current operator (60%) along with Sinochem (40%).

2.3. Aspen Plus® V11 process design

Process was designed to represent a large 400 kbbl.day⁻¹ refining unit (the largest in Brazil) (Fig. 1), with wide range of products output (e.g., LPG to asphalt). T5vol% and T95vol% were defined, in °C, as: untreated LPG (IBP – 32), Light Unstabilized Naphtha (LUN) (32 – 193), Heavy Unstabilized Naphtha (HUN) (85 – 193), Kerosene (KER) (193 – 271), Diesel (DSL) (271 – 350), Atmospheric Gasoil (AGO) (350 – 425), Light Vacuum Gasoil (LVGO) (425 – 510), Heavy Vacuum Gasoil (HVGO) (510 – 565) and Vacuum Residue (VCR) (565 – FBP).

Several sources were used for simulation settings.^{69,70,71} Top and side distillates flowrates were varied to achieve maximum product flowrates flowrates, subject to each product T95 %vol +/- 5 °C for light and medium blends and T95 %vol +/- 15 °C for heavy blends. In this work, no heat integrations were designed, although total energy performances were evaluated

Desalting unit was designed as a liquid-liquid equilibrium separation stage, focused on water and water-soluble components removal. Wash water was fed to the system, which liquid flow was minimized by monitoring input blend water content to achieve 5 vol% water in total mixture. Pre-Flash Unit (PFU) was modelled with 10 stages to improve refinery yields and economics^{72,73,74}, recovering Untreated LPG and Unstabilized Naphtha (LUN). The naphtha stabilization process was not designed in this work. Crude Distillation Unit (CDU) was designed with 35 stages, three side strippers and three pumparounds, recovering Heavy Unstabilized Naphtha (HUN), Kerosene (KER), Diesel (DSL) and Atmospheric Gasoil (AGO) fractions. Wet Vacuum Distillation Unit (VDU) was designed with 9 stages, top total vapor condenser (vacuum system), two pumpbacks and two pumparounds, producing Light Vacuum Gasoil (LVGO), Heavy Vacuum Gasoil (HVGO) and Vacuum Residue (VR) fractions.

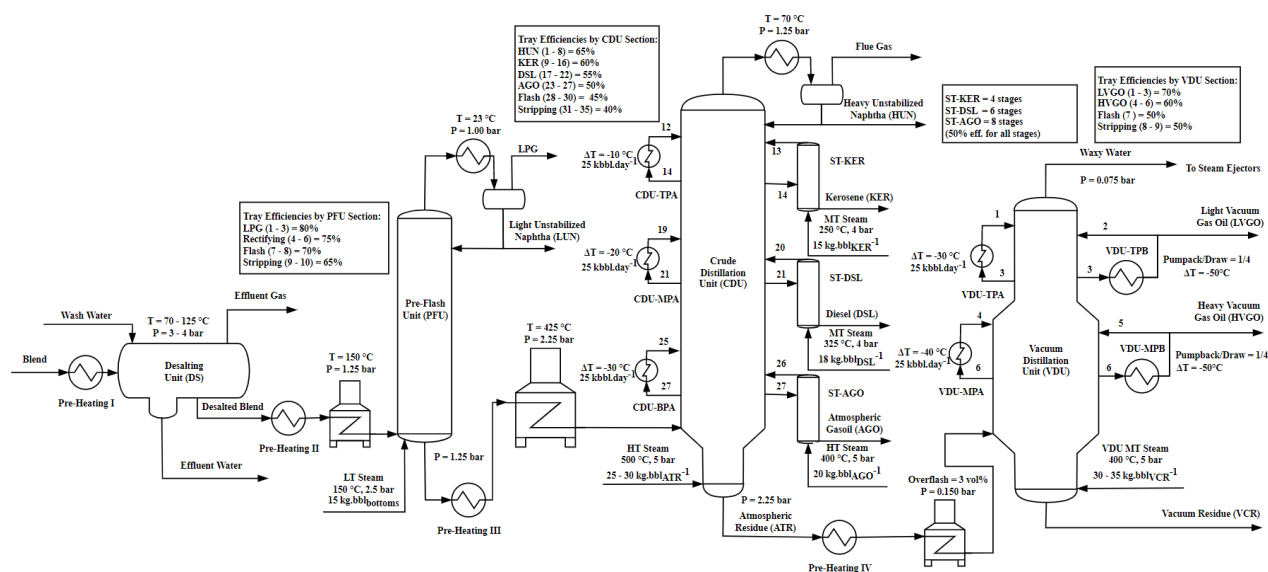


Fig. 1 Process Flow Diagram of Aspen Plus® Simulation Scenarios

3. Results and discussion

3.1. Surrogate eucalyptus fast pyrolysis bio-oil (FPBO) and Brazilian crude oils

FPBO modelled was analyzed in Aspen Plus® generating the distillation curve present in Fig. 2. In the same plot, extended Mante et al. (2016) and Varma et al. (2019) data are compared with EUC24 (24 wt.% water) bio-oil modelled. Literature data existent on bio-oil, however, only presents catalytic fast pyrolysis of pine (Mante et al., 2016, in temperatures A = 425 °C and B = 465 °C) and conventional fast pyrolysis of cedar (Varma et al., 2019), both softwoods that differs from eucalyptus hardwood.

EUC24 presented higher distillation similarities with cedar wood bio-oil, in non-catalytic pyrolysis conditions, presented by Varma et al. (2016). The highest differences can be observed in T10-30vol.% range, affected primarily by water content, and in T95-T100vol.% range, directly correlated to the heavy model compounds used, which also impacted reported viscosity.

EUC24 presented H/C = 1.403 and O/C = 0.433, while Mante et al. (2016) reported H/C = 1.193/1.233 and O/C = 0.357/0.239 (38.89%/94.96% difference from EUC24), and Varma et al. (2019) H/C = 1.469 and O/C = 0.437 (5.41% average difference from EUC24). Molar ratios, along with water and nitrogen contents, also indicates more similarity to cedar oil in terms of composition, which can be explained by the fact that catalytic bio-oil has improved quality presenting lower O/C and N/C ratios, focusing on hydrotreatment processes, however, it decreased energetic potential by also partially reducing H/C ratio.⁷⁵

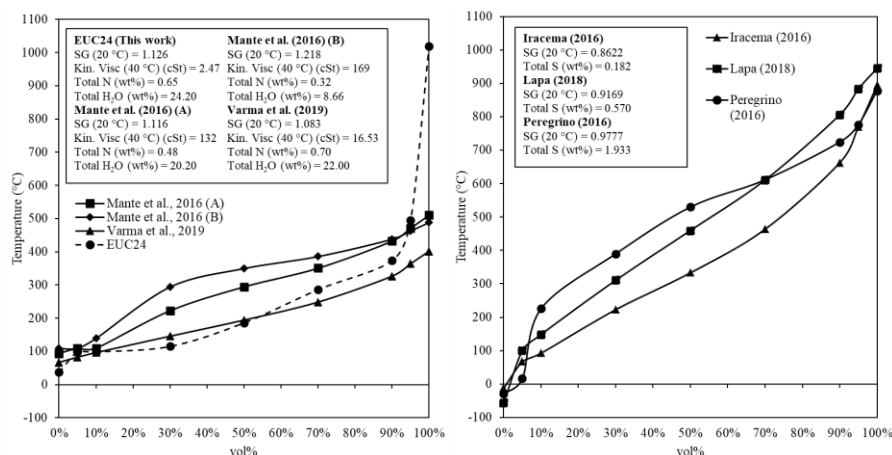


Fig. 2 Distillation curves of eucalyptus bio-oil EUC24 (this work) and literature pinewood catalytic bio-oil (Mante et al., 2016) and cedarwood bio-oil (Varma et al., 2019) (left) and selected crude oils (right).

3.2. Co-processing Analysis

As expected, phase separation occurred, dividing part of the renewable feed. This 2-phase system was formed in the desalting unit, with highest biogenic carbon losses in heavier blends (53.2 and 58.2%, 5% and 10% blends, respectively). Intermediate blends presented the lowest losses, (51.6 and 56.3%) which could be explained by molecular similarities to EUC24's (8 carbons in avg.), preventing phase migration.

This hypothesis was supported by the relative distribution of renewable carbon recovery (Table 1), which showed an average of 10.8% renewable content recovered in LUN, HUN and KER fractions (C5 – C16), especially in HUN (15.7%). Although present in all types of blends, this compatibility is potentially more recurrent with intermediate crudes, with higher renewable content present scattered along different fractions. This effect, however, has a challenge that is the reduction of renewable percentage in the fraction, e.g., intermediate blends have relative recovery percentages above 10% in LUN, HUN and KER, but renewable content in these products is significantly lower than in heavier blends (avg. 11.5 wt.% vs 19.9 wt.%). Therefore, there are opportunities to improve simulations regarding prediction of actual value added by biogenic carbon given a specific input of renewables, a tool of great value towards carbon credits pricing.

Table 1. Relative renewable content (wt.% from total recovered) achieved in each scenario (excluded total fossil scenarios)

Scenario	LPG	LUN	HUN	KER	DSL	AGO	LVGO	HVGO	VCR	Ren. Output (tonne.day ⁻¹)	Ren. Input (tonne.day ⁻¹)	Recovery (%)
L095R005	28.98	5.08	5.51	5.22	1.04	2.29	0.24	0.52	0.44	1293.90	2727.26	47.44
L090R010	37.33	9.51	9.02	9.36	2.14	5.21	0.22	1.07	0.93	2335.92	5454.52	42.83
M095R005	16.05	10.83	8.50	6.71	1.43	1.88	0.05	0.42	0.24	1316.48	2727.26	48.27
M090R010	27.63	16.32	10.31	16.25	4.02	3.81	0.08	0.79	0.50	2371.04	5454.52	43.47
H095R005	4.66	16.44	22.58	7.74	1.05	2.58	0.08	0.15	0.23	1230.43	2727.26	45.12
H090R010	8.75	22.05	31.04	19.56	2.80	4.90	0.23	0.33	0.48	2201.67	5454.52	40.36

Significant changes in energy input and capacity were also observed (Fig 3.) Capacity impacts are linked directly with desalting performance, followed by type of crude since lower density fluid (crude) was replaced by higher density biocrude. Also, since the same conditions were used in all scenarios, efficiency is another source of impact. This fact led to considerable increases in input energy per barrel of product, as water content, although controlled below 0.5 wt.% demanded higher energy inputs.

Intermediate blends distribution effect mentioned collaborated to reduce this energy increase. It has been seen that overall energy input was lower than other blends, as well as lower difference in energy input between scenarios including renewable oil. Optimal blending ratios and identification of the key components responsible for the increase of this energy input are opportunities to understand how to improve coprocessing financial and operational viability.

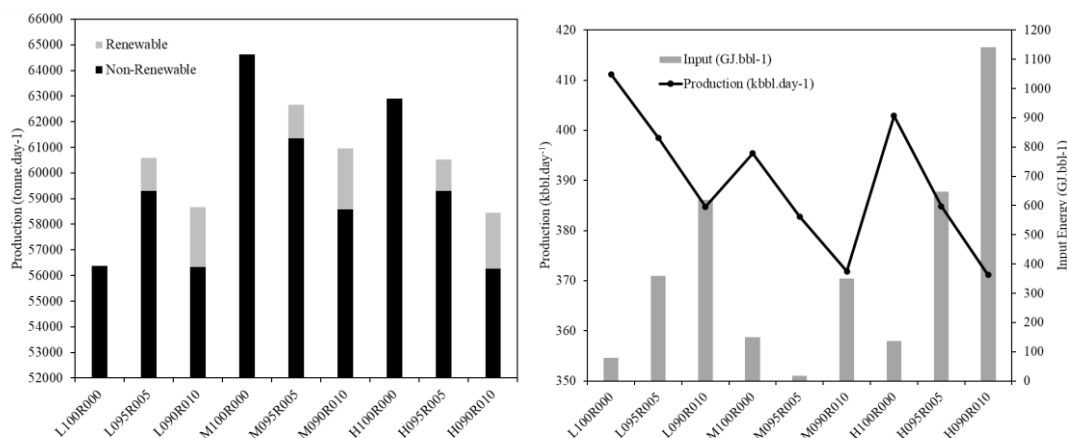


Fig. 3 Renewable production on each scenario simulated (left) and energy input relative to the sum of products volume (right).

4. Conclusions

Coprocessing is one of the most promising routes for renewable fuels and chemicals in the near future. Policies and research fundings in Brazil are focusing on enabling advanced coprocessing biofuels for carbon credits emission eligibility. This study has shown part of this development, with the concrete modelling of eucalyptus bio-crude, one of main species in the country, which matched several properties from experimental data. Further development is needed towards viscosity values, which depends highly on heavy unknown components. Also, with the Aspen Plus® simulations of coprocessing with Brazilian crude oils, it was seen that pre-salt medium °API was of excellent combination, providing up to 10 wt.% biogenic carbon presence in light and heavy naphtha and kerosene fractions. However, improvements are still needed, as almost 50 wt.% of renewable content is lost in desalting phase separation and heat integrations are on development to validate the tool as a reliable virtual sensor for renewable carbon.

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