



Full Length Article

Limitations in the energy balance when VGO/aqueous bio-oil mixtures are co-processed in FCC units

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ARTICLE INFO

Keywords:

Catalytic cracking
Aqueous bio-oil
FCC simulation
Regenerator
Coke

ABSTRACT

The effect on the energy balance of a FCC unit after co-feeding the aqueous fraction of a bio-oil together with a vacuum gas oil (VGO) has been studied. The simulation program considers the interdependency relationship between the reaction and regeneration sections in the unit, where the heat of coke combustion has to sustain the energy requirements to preheat and vaporize the feedstock as well as the endothermic cracking reactions. The combustion of coke deposited on an equilibrium commercial FCC catalyst in cracking various bio-oil/VGO mixtures at 530 °C, with catalyst to oil relationships between 3 and 6 in a CREC Riser Simulator laboratory reactor, was investigated by means of thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC).

Results showed that the heat from coke combustion is not enough to provide the energy needed in the unit when the amount of bio-oil in the feedstock is larger than 5 wt%, mainly due to the high content of water in the aqueous fraction of the bio-oil and to the lower heat of combustion of the coke formed in co-processing, as compared to the VGO alone.

1. Introduction

Important actions are being taken at present days about the substitution of fossil fuels for more sustainable sources. One of the strategies which is receiving more attention is the incorporation of lignocellulosic biomass in biorefinery platforms. In this way, “green” fuels and high value chemicals can be obtained, thus decreasing oil consumption rates and greenhouse gas emissions [1,2].

Bio-oils constitute a very interesting biorefinery platform. They are liquids derived from the pyrolysis of lignocellulosic biomass after simple technologies with low environmental impact [3], which can be further upgraded into renewable fuels or mixed with fossil fuels, following various routes [4,5].

Bio-oils are composed by a large number of oxygenated compounds having very different chemical functionalities (acids, alcohols, aldehydes, phenolic compounds, sugars, pyrolytic lignin) as well as important amounts of water, from 15 to 70 % [6,7]. Differently from oil derived fuels, bio-oils have a low content of nitrogen and sulfur, but cannot be directly used as fuels given their high content of oxygen and

water, low calorific value, viscosity (10–100 cP at 40 °C), acidity (pH 2–4), corrosive nature and poor storage properties [8,9]. Various processes, both physical and chemical, have been developed to neutralize these problems in the use of bio-oils as fuels [10–12]. However, they are typically expensive and/or decrease the yield to desired products in further catalytic upgrading.

A promising strategy to obtain fuels from bio-oils is co-processing them with usual feedstock streams in refinery units. The main advantage from this approach is that it is not necessary to develop new processes and, consequently, since units are active and fully amortized, important savings in capital costs are obvious. It can be assumed that the cost of fuels from co-processed bio-oil would be similar to that of crude oil derived fuels, depending on the characteristics of the bio-oils and the contents under which they are co-processed [13–15].

Among the different possible options, the fluid catalytic cracking (FCC) and the hydrocracking technologies are feasible [16,17] but, given its singular and versatile nature, FCC units are more appropriate to co-process bio-oils together with their typical feedstocks, vacuum gas oils (VGO). Studies exist which have shown the technical viability of this

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co-processing [14,15,18–21]. These studies include the cracking of oxygenated model compounds [22,23], mixtures of oxygenates with VGO [24–27], thermally aged bio-oils [28], bio-oils obtained from catalytic pyrolysis [29] and aqueous fractions of bio-oils, which do not contain most of the phenolic compounds [30]. In co-feeding up to 15 wt % of bio-oil in the mixture, product yields were similar to those of cracking VGO alone, the yield of oxygenates being almost negligible [31]. However, when 20 wt% of bio-oil is co-fed, the results are different, a decrease in gasoline yields being observed from 39 to 42 wt % in VGO cracking down to 36–38 wt% in mixture cracking [32]. Ibarra et al. [33–37] studied the cracking of raw bio-oil together with VGO, showing synergy between the cracking mechanisms of oxygenates and hydrocarbons, as well as an important decrease in coke yield, given the water contributed by bio-oil to the reaction medium.

Coke formation has a special relevance in the heat balance of the reactor-regenerator system of FCC units, as it controls the amount of heat that is produced from its combustion in the regenerator section. Coke yields when bio-oil and a hydrocarbon cut are cracked simultaneously differ significantly, depending on the raw biomass, the type of reactor, the catalyst and the temperature range in the experiments. For example, Shimada et al. [38], who cracked mixtures with 20–30 % Japanese cedar bio-oil and VGO at temperatures between 450 and 500 °C in a MAT reactor with a partially deactivated commercial resid FCC catalyst, reported that coke yield increased if bio-oil was co-processed. Similar results were published by Santillán-Jiménez et al. [39] after cracking 10% bio-oil from the hydrothermal liquefaction (HTL) of microalgae mixed with VGO at 520 °C in a MAT reactor. However, Pujro et al. [40] found that coke yield decreased in the cracking of oxygenated model compounds (phenol, syringol or trimethoxybenzene) dissolved in tetralin (50%) in a batch fluidized bed, riser simulator reactor at 500 °C. Wang et al. [20] cracked mixtures of untreated and hydrotreated pyrolysis oils from pine wood and VGO (10 % bio-oil) in a pilot scale FCC riser reactor at 525 °C and observed lower coke yields as compared to the processing of VGO only.

Ibarra et al. [34] observed significant differences in the coke formation mechanisms when raw bio-oil and VGO were cracked concurrently in a riser simulator reactor in the 500–550 °C range. While coke from VGO hydrocarbons is constituted by ordered polycondensed aromatic nanostructures, oxygenated compounds in bio-oils tend to form lighter coke containing oxygen, which is less ordered and more aliphatic in nature.

It can also be noticed that the occurrence of water in bio-oils has an important attenuation effect on both coke deposition mechanisms. This effect also explains the difference in the resulting coke yield, its nature and the deactivation consequences on the catalyst and the product distribution in the co-processing of bio-oil obtained from different biomass sources [36].

Most of the papers aimed at studying the co-processing of bio-oils and VGO in FCC units reported the effects on conversion, product yields and emissions, but no attention was given to heat balances in the units, which are crucial to their operation. Both water content in the bio-oil and coke on catalyst have a strong influence on the heat balance. Even though energy is required to vaporize the bio-oil when water is present, a number of reasons can be mentioned to support the interest in valorizing bio-oils without dewatering. For example, expensive technologies, such as membranes, would be required to avoid heating, which produces bio-oil aging leading to the deposition of large amounts of carbonaceous materials (pyrolytic lignin). Moreover, it is a common practice in FCC units to inject steam to ease feedstock vaporization and further cracking. The stripping section between reactor and regenerator provides a countercurrent contact between steam at high temperature and catalyst particles aimed at removing volatile hydrocarbons adsorbed on the catalyst surface. It has also been shown in the conversion of bio-oil that moderate water concentrations attenuate coke deposition [33–37], thus allowing the catalyst to maintain higher activity. Consequently, it could be convenient to co-process bio-oils in refineries

without previous dewatering.

Bhatt et al. [41] analyzed the capacity and technological drawbacks of USA refineries and the effect of co-feeding various bio-oil/VGO ratios on refinery emissions. The study was based on information from the National Renewable Energy Laboratory (NREL), embracing 55 out of 95 refineries which could co-process 20 % bio-oils – VGO mixtures without significant reforms. Another 34 refineries could co-process 4 to 20% bio-oils – VGO, while only 6 refineries would need important modifications to obey environmental laws. Thus, 573,000 bio-oil barrels could be co-processed daily, representing about 1.92 billions of equivalent gasoline gallons a year.

If bio-oil is co-processed, the heat balance of the unit will be modified as coke from the cracking of the mixtures is different in nature and yields [18,33,42–44] and thus will have an effect on regenerator temperature. If the reactor temperature is to be controlled, given the interdependency relationship between conditions in the reaction and regeneration sections in FCC units, VGO preheating and reactor's input temperatures or the catalyst/feedstock C/O ratio should be modified in case bio-oils are co-processed.

It is the objective of this work to study the effect of co-processing a bio-oil and a conventional VGO on all the variables which occur in the heat balance of a commercial FCC unit. In this way, it is possible to determine the maximum acceptable content of bio-oil and the consequences on the energy balance. The simulation of the performance of a FCC unit was performed at various bio-oil contents in the feedstock, keeping the total mass flow unchanged and considering the experimental information from the conversion of mixtures at the laboratory under commercial process conditions.

2. Experimental

The experimental information needed to perform the simulation of the FCC unit was gathered from laboratory experiments of catalytic cracking where, in order to determine coke yields and the corresponding coke heating values, VGO and bio-oil were co-processed at various relationships under conditions similar to those in a refinery.

2.1. Feedstocks

The bio-oil was obtained from the pyrolysis of mesquite sawdust. It was pyrolyzed at 600 °C during 30 min, under N₂ flow of 80 cm³/min. The yields of the char, liquid and gas product phases are shown in Table 1. During the pyrolysis of mesquite sawdust bio-oil, gas and char products are obtained and the sum of their yields equals to 100 wt%. The bio-oil, however, consists of aqueous phase and tar, their respective yields being equal to the yield of the bio-oil.

Detailed information about the experimental pyrolysis procedure can be found in previous papers, e.g., [45,46].

The aqueous phase of bio-oil was used in the experiments. Its most important properties are shown in Table 2. Table 3 shows the concentration of the main organic components in that aqueous phase. Table 4 shows the most important properties of the VGO.

2.2. Catalyst

A FCC commercial equilibrium catalyst was used, which was

Table 1
Yields in the pyrolysis of mesquite sawdust at 600 °C.

Product phase	Yield, wt%
Bio-oil	59.6
Aqueous phase	48.5
Tar (viscous phase)	11.1
Char	23.7
Gas	16.7

Table 2
Properties of the aqueous phase of bio-oil.

Property	
pH	3
Density, g mL ⁻¹	1.06
Water content, wt% ^a	74.5
Elemental composition, wt%	
C	13.67
H	10.10
N	0.21
O ^b	76.02

^a Karl-Fischer method.^b Calculated by difference.**Table 3**
Main organic components in the aqueous phase of bio-oil.

Components	wt%
Acids	24.26
Esters	12.40
Aldehydes	2.93
Alcohols and sugars	15.46
Ketones	17.23
Alkylated Phenols	6.74
Phenols ethers	11.65
Furans	5.73
Ethers	1.26
Hydrocarbons	0.14
Unknown	2.20

Table 4
Properties of the VGO.

Property	
API (°)	22.94
Conradson Carbon, wt%	0.17
Simulated distillation, °C ^a	
Initial	226
10 wt%	361
30 wt%	408
50 wt%	432
70 wt%	456
90 wt%	494
95 wt%	513
Final	539
Nickel, ppm	0.10
Vanadium, ppm	0.73
Sodium, ppm	0.38
Iron, ppm	2.36
Copper, ppm	< 0.02

^a ASTM D-2887 Standard.

provided by Petronor S.A. (Muskiz, Bizcay, Spain). The catalyst was formulated to maximize the yield of gasoline. Its most important properties are shown in Table 5.

2.3. Reactor set up and product analysis

The experiments of catalytic cracking were performed in a CREC Riser Simulator reactor [47], which can be operated at the laboratory scale under conditions similar to those in commercial FCC units. Fig. S1 in Supporting Information shows a schematic representation of the set up.

The reactor contains a catalyst basket between two porous metal plates, which retain the catalyst during fluidization induced by the internal high gas recirculation from an impeller. After the reaction time has elapsed, which is equivalent to contact time in the riser reactor, the reactor is connected with a vacuum chamber to immediately evacuate

Table 5
Catalyst properties.

Property	
BET Specific surface area, SBET, m ² g ⁻¹	100
Micropore specific surface area, S _{micro} , m ² g ^{-1 a}	62
Mesopore specific surface area, S _{meso} , m ² g ⁻¹	38
Total pore volume, TPV, cm ³ g ⁻¹	0.1034
Micropore volume, V _{micro} , cm ³ g ⁻¹	0.0025
Mesopore volume, V _{meso} , cm ³ g ^{-1 a}	0.1009
Average mesopore diameter, Å	41.25
Zeolite content, wt%	10.11
Rare earth content, wt% ^b	1.59
Zeolite unit cell size, Å ^c	24.29
Fe, wt%	0.45
Ni, wt%	0.076
V, wt%	0.28

^a S_{micro} = S_{BET} - S_{meso}; V_{micro} = TPV - V_{meso}.^b Rare earth oxides.^c ASTM D3942-85.

the reaction products and analyze them.

The experiments were performed with bio-oil/VGO mixtures having from 0 to 100 wt% bio-oil at the constant temperature of 530 °C, reaction time of 10 s and using three catalyst/feedstock relationships (C/O, 3, 4.5 and 6 g_{cat} g_{feed}⁻¹).

The reaction products were analyzed in an Agilent Technologies 6890 N gas chromatograph with FID detection. Hydrocarbons can be grouped into dry gas (normal boiling point < -48 °C), liquefied petroleum gas (LPG) (-48 - 30 °C), gasoline (30 - 212 °C) and light cycle oil (LCO) (212 - 343 °C) groups and unconverted hydrocarbons (>343 °C). Results from the experiments are shown in Supporting Information.

The yield of each product lump was calculated by means of the following expression.

$$Y_i(\%) = \frac{m_i}{m_{feed}} 100 \quad (1)$$

where m_i and m_{feed} are the mass of lump i and the mass of the feedstock, respectively. Conversion was defined as.

$$X(\%) = Y_{Drygas} + Y_{LPG} + Y_{Gasoline} + Y_{Coke} \quad (2)$$

After repeatedly performing the experiments under the same conditions, it was possible to determine that the relative error in the results is lower than 2 %.

The amount of coke on the catalyst was determined by means of its controlled combustion in a thermogravimetric equipment (TGA-Q 5000 de TA Instruments), using a heating rate of 5 °C min⁻¹ from 200 °C to 650 °C and an air flowrate of 40 cm³ min⁻¹. The coke content is referred to the catalyst mass, according to:

$$C_C = \frac{m_{coke}}{m_{catalyst}} 100 \quad (3)$$

The heating value of coke was determined with differential scanning calorimetry (DSC) in a TG-DSC 111 equipment from Setaram, using a heating rate of 5 °C min⁻¹ from 150 °C to 650 °C, nitrogen flowrate of 30 cm³ min⁻¹ and air flowrate of 30 cm³ min⁻¹.

3. FCC unit simulation

The experimental data gathered at the laboratory were used in the simulation of a commercial FCC unit. The detailed description of the model used can be found in, e.g., [48,49].

The simulation of the regenerator unit considers the description of gas flows as reported by de Lasa et al. [50], and the amount of catalyst entrained is calculated using the method by George and Grace [51].

Fig. 1 shows a schematic representation of the simulated FCC unit. Both the characteristics of the VGO feedstock and the unit are shown in Table 6. The most important operating parameters are shown in Table 7.

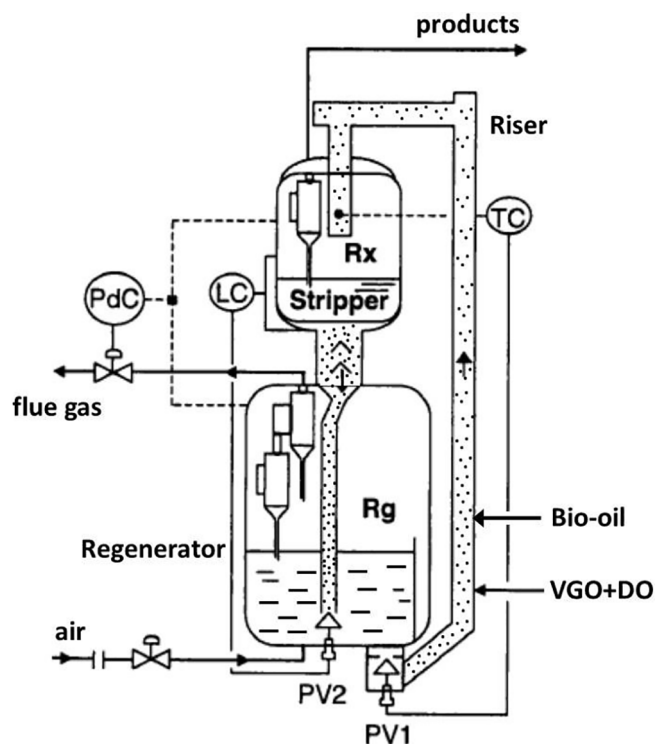


Fig. 1. Schematic representation of the simulated FCC unit.

Table 6
Characteristics of the simulated FCC unit and VGO properties.

<i>Riser</i>	
Diameter, m	0.96–1.25
Height, m	32.7
<i>Regenerator</i>	
Diameter, m	9.4
Height, m	3.4–12.5
Catalyst holdup, tonnes	120
<i>Feedstock properties</i>	
Distillation	ASTM D1160
30 vol%	400 °C
50 vol%	430 °C
70 vol%	460 °C
90 vol%	512 °C
Sulfur	0.69 wt%
Conradson Carbon	0.11 wt%
Viscosity (100 °C)	16 cS
Aniline Point	90 °C

When part of the VGO is substituted for bio-oil some of the operation's parameters change. The most important parameters which affect the heat balance of the unit are the coke yield, the specific heat capacity of cracking products, the heating value of coke and the heat of cracking reactions. Table 8 shows those values when VGO (reference) or the various bio-oil/VGO relationships are used in the simulations of the FCC unit.

The yields of coke shown in Table 8 were obtained from the laboratory experiments at $C/O = 6$. The heating value of the coke formed from the various bio-oil/VGO mixtures was calculated from the combustion heat of coke formed from VGO alone, multiplied by factors according to the composition of the mixtures. The factors, in turn the result of dividing the heating value of coke from VGO alone by the heating values of the different cokes from the mixtures (see Fig. 4), are included in Table 8. For example, the factor corresponding to the case of 10 wt%

Table 7
Operating parameters used in the simulation of the FCC unit.

Parameters	
VGO flow rate, kg s^{-1}	59.77
VGO preheating temperature, °C	223
Recirculated decanted oil (DO) flow rate, kg s^{-1}	2.06
Recirculated decanted oil (DO) temperature, °C	316
Catalyst flow rate, kg s^{-1}	425
Mixing point temperature, °C	547.7
Riser top temperature, °C	510
Stripping steam flow rate, kg s^{-1}	1.27
Stripping steam temperature, °C	300
Riser pressure, atm	1.72
Coke yield, wt%	6.00
Regenerator air flow rate, kg s^{-1}	60.58
Regenerator air temperature, °C	157
Regenerator dense phase temperature, °C	696.4
O_2 concentration in the flue gas (dry basis), %	5.13

bio-oil/90 wt% VGO is 0.9330, showing that the heating value of the coke produced by the mixture represents a fraction of the case of coke from the VGO.

The air flowrate used in the simulations was calculated to maintain the concentration of oxygen at the value observed when 100 wt% VGO is used (5.13 %).

Two different types of simulations were performed, the objective being to maintain the riser temperature constant at 510 °C. This can be achieved by keeping the C/O ratio constant, thus using a different preheating temperature as a function of the bio-oil content in the mixture. The other choice is to maintain the preheating temperature of the feedstock constant and change the C/O ratio. It is common practice in FCC units to control the riser exit temperature by acting the slide valve which controls the catalyst flow rate from the regenerator, thus making the second option seem more realistic. However, this a dynamic situation where changes are moderate. In this case this is not a control move to cancel a perturbation or a response to a variation in a set point, but a modification to define a new operative condition in the unit, corresponding to a significant change in the feedstock. Thus, it is important to study both options, considering that no significant changes in the unit's control structure are to be produced.

4. Results and discussion

4.1. Effect of co-processing bio-oil and VGO on coke yield and properties

In order to obtain fundamental conclusions, the complete range of bio-oil contents (0–100 wt%) was analyzed.

Fig. 2 shows the amount of coke on catalyst as a function of the content of bio-oil in the mixture with VGO, for the three C/O ratios studied. It can be seen that the amount of coke and consequently its yield (see Fig. 3) decrease as long as the content of bio-oil in the feedstock increases for a given C/O at this reaction temperature.

Fig. 4 shows the coke heating values as a function of the content of bio-oil in the feedstock, for all the C/O ratios used. It can be seen that the heating value decreases as the amount of bio-oil increases. This can be assigned to the lower content of carbon and hydrogen in the coke, as it contains more oxygen, when bio-oils are co-processed in higher contents. It can also be observed that the coke formed at higher C/O ratios has lower heating values, consistently with the fact that at higher C/O ratios, coke is more condensed, with lower hydrogen content.

In order to show the effect of the C/O relationship on the coke heating value, Fig. 5 shows the DSC profiles of the samples corresponding to the mixture with 60 wt% bio-oil cracked at C/O ratios of 3 and 6. It can be seen that the coke formed at $C/O = 3$ starts burning at temperatures higher than 300 °C, while the coke corresponding to $C/O = 6$ starts burning at about 400 °C. Moreover, the maxima in the profiles arise at different temperatures, indicating that the coke produced at the

Table 8

Parameters used in the simulation of the FCC unit with the different feedstocks.

Feedstocks	Coke yield, wt%	Cp prod., kcal kg ⁻¹ °C ⁻¹	Coke heating factor	Air flowrate, kg s ⁻¹	Mixture heat of cracking, kcal kg ⁻¹ ^a
VGO	6.00	0.8200	1	60.58	140
Bio-oil, 5 wt%	5.79	0.8236	0.9668	58.06	132.0–134.8
Bio-oil, 10 wt%	5.40	0.8272	0.9330	53.60	124.0–129.6
Bio-oil, 20 wt%	4.83	0.8344	0.8862	47.00	107.9–119.1
Bio-oil, 40 wt%	4.23	0.8487	0.8280	39.90	75.9–98.2
Bio-oil, 60 wt%	3.64	0.8631	0.7136	32.60	43.8–77.4
Bio-oil, 80 wt%	3.10	0.8775	0.6215	26.20	11.7–56.5
Bio-oil, 100 wt%	2.64	0.8918	0.5248	21.25	–20.4–35.7

^a The values represent the limits imposed by the different assumptions in relation to the heat of cracking of bio-oil (see text below).

lowest C/O is the lightest.

4.2. Constant C/O ratio

Table 9 shows the results obtained in the simulation when only VGO is fed to the unit (reference situation).

It can be seen that in this case the VGO preheating temperature is 223 °C; in this way, when mixing with the hot catalyst from the regenerator at 696.4 °C, the temperature at the riser bottom is 548 °C. The temperature profile along the riser decreases as long as the catalytic cracking reactions proceed, given their endothermic nature, reaching the set final temperature of 510 °C.

It was assumed in the heat balance in the mixing point of regenerated hot catalyst and feedstocks that bio-oil is fed liquid at 40 °C, its heat of

vaporization being calculated after the following equation:

$$\Delta H_{vap} = 539.1 x_{steam} + (1 - x_{steam}) 145.7 \text{ kcal kg}^{-1} \quad (4)$$

where x_{steam} is the mass fraction of water in the bio-oil and 145.7 kcal kg⁻¹ is the heat of vaporization of bio-oil on a dry basis [52]. Moreover, the heat capacity of bio-oil is 0.58 kcal kg⁻¹ °C⁻¹ [52].

The heat of bio-oil cracking has not been reported in the literature. Jarvis et al. [53] showed that the heat of reaction of bio-oil model compounds, such as acetic acid, guaiacol, and sorbitan monooleate is

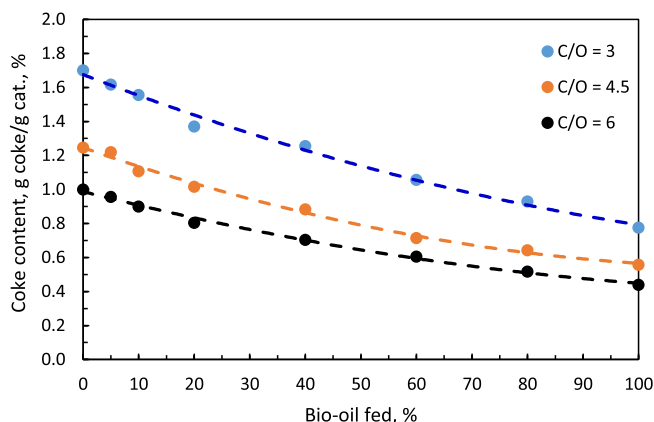


Fig. 2. Coke content on catalyst as a function of the content of bio-oil in the feedstock for various C/O ratios. T = 530 °C, reaction time = 10 s.

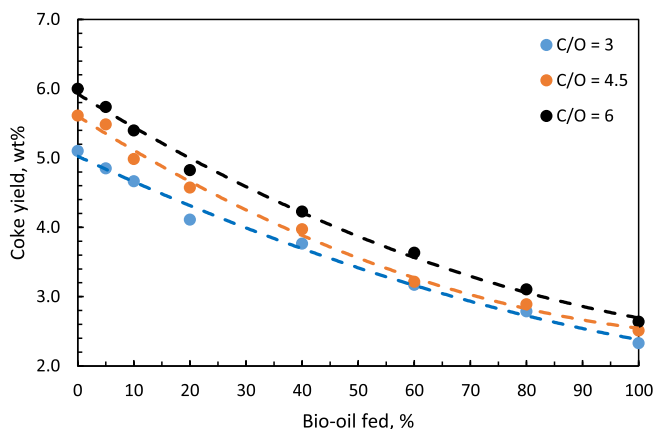


Fig. 3. Coke yield as a function of the content of bio-oil in the feedstock for various C/O ratios. T = 530 °C, reaction time = 10 s.

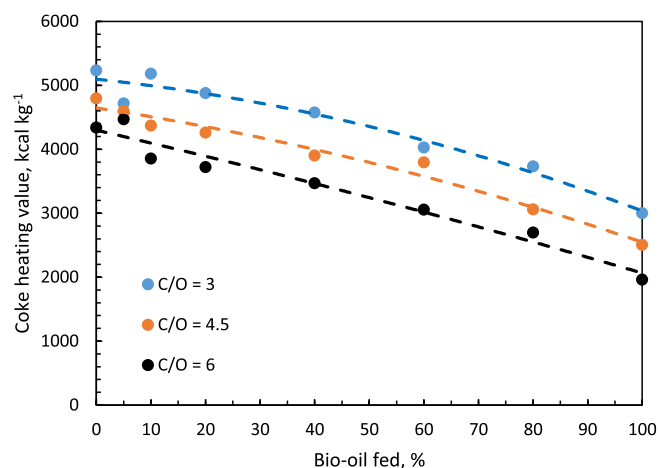


Fig. 4. Coke heating value as a function of the content of bio-oil in the feedstock for various C/O ratios. T = 530 °C, reaction time = 10 s.

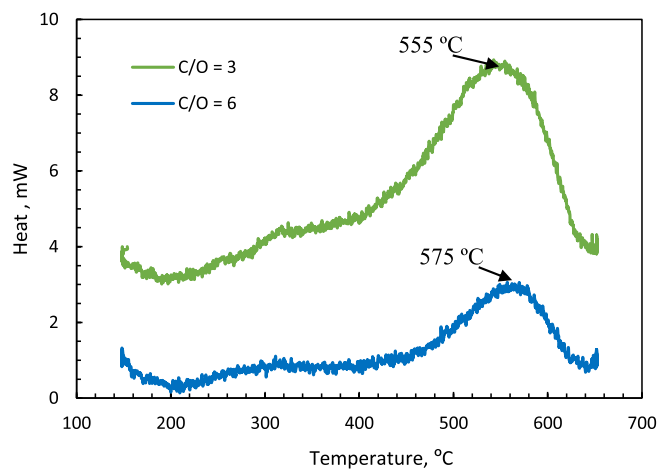


Fig. 5. DSC profiles of coke obtained in the cracking of the feedstock containing 60 wt% bio-oil. T = 530 °C, C/O ratios: green line (C/O = 3), blue line (C/O = 6). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 9

Results of the unit simulation when only VGO is the feedstock.

Conditions	
Regenerator temperature, °C	696.4
Concentration of O ₂ in the flue gas, % (dry basis)	5.13
Mixing point temperature, °C	548
Heat provided by the regenerated catalyst, kcal s ⁻¹	15,809
Heat given to VGO, kcal s ⁻¹	15,339
VGO preheating temperature, °C	223

slightly endothermic or even exothermic. Then, various scenarios have been approached in the simulation.

Considering results from [53], the following heats of bio-oil cracking (dry basis) were assumed: A, 140 kcal kg⁻¹; B, 100 kcal kg⁻¹; C, 60 kcal kg⁻¹; D, 0 kcal kg⁻¹ and E, -80 kcal kg⁻¹. Case A would be the same as the VGO heat of cracking. Cases B and C correspond to situations where the heat of reaction would be endothermic, but lower than that of VGO. Cases D and E are situations where the heat of reaction would be nil and exothermic, respectively.

The heats of cracking of the VGO – bio-oil (water included) mixtures were calculated from the individual heats of cracking (VGO and dry bio-oil) considering the amount of water in bio-oil and the limits provided by the different heats of bio-oil cracking assumed (see Table 8). Results obtained in the simulations corresponding to the various cases (heats of cracking and bio-oils concentrations) are shown in Tables 10–13. ΔH_{VGO} is the difference between the heat required for preheating VGO in the different mixtures and the heat for preheating VGO when no bio-oil is in the feed.

It can be seen that results are similar in all the cases. When bio-oil is co-processed, as the yields of coke and the heating values are lower, a lower amount of combustion heat is available, and even though the combustion air flow rate is lower than that used with VGO only, the temperature in the regenerator decreases. Finally, the heat provided by the regenerated catalyst to the feedstock decreases when the content of bio-oil in the mixture increases.

If the bio-oil heat of cracking is the same as that of VGO, in the case of co-processing the mixture with 5 wt% bio-oil the decrease in the amount of heat provided by the hot catalyst is almost 6 % as compared to the processing of VGO only. The high content of water in bio-oil, which needs to be vaporized, induces the VGO preheating temperature to increase from 223 to 282 °C, almost a 60 °C increase. If the mixture contains 20 wt% bio-oil, the heat provided by the catalyst decreases 27 % and the VGO preheating temperature goes to 475 °C, that is, more than a 250 °C increase. Then, co-feeding 20 wt% crude bio-oil could be

Table 10

Simulation results for the processing of 95 wt% VGO – 5 wt% bio-oil mixture assuming different values for the dry bio-oil cracking heat.

	Heat of dry bio-oil cracking, kcal kg ⁻¹				
	140	100	60	0	-80
Mixture cracking heat, kcal kg ⁻¹	134.8	134.3	133.8	133.0	132.0
Regenerator temperature, °C	686.6	686.6	686.6	686.6	686.6
O ₂ concentration in flue gas (dry basis), %	5.11	5.11	5.11	5.11	5.11
Coke on regenerated catalyst, wt%	0.036	0.036	0.036	0.036	0.036
Mixing point temperature, °C	546.1	545.9	545.9	545.6	545.3
Heat provided by regenerated cat., kcal s ⁻¹	14,926	14,940	14,954	14,978	15,007
Heat provided to bio-oil, kcal s ⁻¹	2190.2	2190.0	2189.7	2189.5	2189.1
Heat provided to VGO, kcal s ⁻¹	12,289	12,304	12,317	12,343	12,372
VGO preheating temperature, °C	281.7	281.1	280.7	279.8	278.7
ΔH_{VGO} , kcal s ⁻¹	1745	1724	1708	1672	1629

Table 11

Simulation results for the processing of 90 wt% VGO – 10 wt% bio-oil mixture assuming different values for the dry bio-oil cracking heat.

	Heat of dry bio-oil cracking, kcal kg ⁻¹				
	140	100	60	0	-80
Mixture cracking heat, kcal kg ⁻¹	129.6	128.5	127.5	126.0	124.0
Regenerator temperature, °C	671.4	671.5	671.5	671.5	671.5
O ₂ concentration in flue gas (dry basis), %	5.11	5.11	5.11	5.11	5.11
Coke on regenerated catalyst, wt%	0.041	0.041	0.041	0.041	0.041
Mixing point temperature, °C	544.5	544.3	544.0	543.6	543.0
Heat provided by regenerated cat., kcal s ⁻¹	13,483	13,514	13,543	13,586	13,645
Heat given to bio-oil, kcal s ⁻¹	4375.2	4374.2	4373.3	4371.8	4369.9
Heat given to VGO, kcal s ⁻¹	8689	8721	8752	8796	8857
VGO preheating temperature, °C	355.8	354.8	353.7	352.2	350.1
ΔH_{VGO} , kcal s ⁻¹	4033	3991	3947	3886	3803

Table 12

Simulation results for the processing of 80 wt% VGO – 20 wt% bio-oil mixture assuming different values for the dry bio-oil cracking heat.

	Heat of dry bio-oil cracking, kcal kg ⁻¹				
	140	100	60	0	-80
Mixture cracking heat, kcal kg ⁻¹	119.1	117.1	115.0	112.0	107.9
Regenerator temperature, °C	649.8	649.8	649.8	649.8	649.8
O ₂ concentration in flue gas (dry basis), %	5.11	5.11	5.11	5.11	5.11
Coke on regenerated catalyst, wt%	0.050	0.050	0.050	0.050	0.050
Mixing point temperature, °C	541.6	541.0	540.5	539.6	538.5
Heat provided by regenerated cat., kcal s ⁻¹	11,498	11,555	11,615	11,703	11,820
Heat given to bio-oil, kcal s ⁻¹	8730	8726	8722	8716	8708
Heat given to VGO, kcal s ⁻¹	2398	2459	2523	2616	2741
VGO preheating temperature, °C	475.2	472.9	470.5	467.0	462.2
ΔH_{VGO} , kcal s ⁻¹	7713	7631	7547	7422	7257

Table 13

Simulation results for the processing of 60 wt% VGO – 40 wt% bio-oil mixture assuming different values for the dry bio-oil cracking heat.

	Heat of dry bio-oil cracking, kcal kg ⁻¹				
	140	100	60	0	-80
Mixture cracking heat, kcal kg ⁻¹	98.2	94.2	90.1	84.0	75.9
Regenerator temperature, °C	626.3	626.3	626.3	626.3	626.3
O ₂ concentration in flue gas (dry basis), %	5.1	5.1	5.1	5.1	5.1
Coke on regenerated catalyst, wt%	0.061	0.061	0.061	0.061	0.061
Mixing point temperature, °C	535.7	534.6	533.6	532.0	529.8
Heat provided by regenerated cat., kcal s ⁻¹	9657	9743	9860	10,029	10,259
Heat given to bio-oil, kcal s ⁻¹	17,378	17,363	17,349	17,326	17,295
Heat given to VGO, kcal s ⁻¹	—	—	—	—	—
VGO preheating temperature, °C	—	—	—	—	—
ΔH_{VGO} , kcal s ⁻¹	—	—	—	—	—

considered an upper limit, as it imposes an extremely high VGO preheating temperature, inducing thermal cracking of the feedstock and an unacceptable energy cost.

As the heat of reaction of the mixture decreases, becoming less endothermic, the hot catalyst provides more energy to the bio-oil-VGO

mixture to maintain the set temperature at the riser reactor exit. Consequently, for a given content of bio-oil in the mixture, the temperature in the mixing point decreases.

In cases where the heat of reaction of the mixture is lower, the decrease in the amount of energy provided by the hot regenerated catalyst as compared to the case of VGO only (see Table 9) becomes smaller. For example, in the case of co-processing 20 wt% bio-oil (see Table 12), the heat provided by the hot catalyst decreases approximately 25 % if the heat of cracking the dry bio-oil is -80 kcal kg^{-1} (exothermic). It can also be observed that, besides the fact that the VGO preheating temperature is higher than that of the case of VGO only, the increase in the preheating temperature is increasingly smaller as the heat of cracking decreases.

The changes in the VGO preheating temperature as a function of the heat of reaction of the mixture magnify with the percentage of bio-oil in the feedstock. Thus, in the case of 5 wt% bio-oil, the difference in the VGO preheating temperature for the extreme cases of the heat of reaction is only $3 \text{ }^\circ\text{C}$, while in the case of 20 wt% bio-oil, the difference is $13 \text{ }^\circ\text{C}$.

As the VGO preheating temperature increases, so do operation costs. Fig. 6 shows the amount of additional power needed to reach the VGO preheating temperature from the $223 \text{ }^\circ\text{C}$ base temperature (case when only VGO is processed), as a function of the content of bio-oil in the mixtures. In these cases the heat of dry bio-oil cracking was assumed the same as that of VGO cracking.

When the feedstock includes 40 wt% bio-oil, the hot catalyst from the regenerator at $626 \text{ }^\circ\text{C}$ cannot provide the amount of energy necessary to increase the temperature of the bio-oil from $40 \text{ }^\circ\text{C}$ to the mixing point temperature, independently from whichever the heat of cracking bio-oil is. The reason for this is the large amount of water in crude bio-oil. In the unit's heat balance it would mean that the VGO should be heated to temperatures much higher than those of reaction, thus inducing its thermal cracking and the deposition of coke in all the elements of the preheating ovens.

It can be concluded from the simulations that, as the heating value and the yield of coke from bio-oil are low, the strategy of maintaining the C/O ratio constant is limited by the amount of bio-oil to co-process. The limit mainly depends on the concentration of water in crude bio-oil. Should the limit be surpassed, besides increasing energy costs to unacceptable values, the VGO (or the bio-oil) should have to be preheated to temperatures at which thermal cracking proceeds.

4.3. Constant preheating temperature

In this case, the C/O ratio in the FCC unit was calculated as a function of the content of bio-oil in the feedstock mixture to maintain the VGO preheating temperature at the value used when VGO is fed alone. Bio-oil

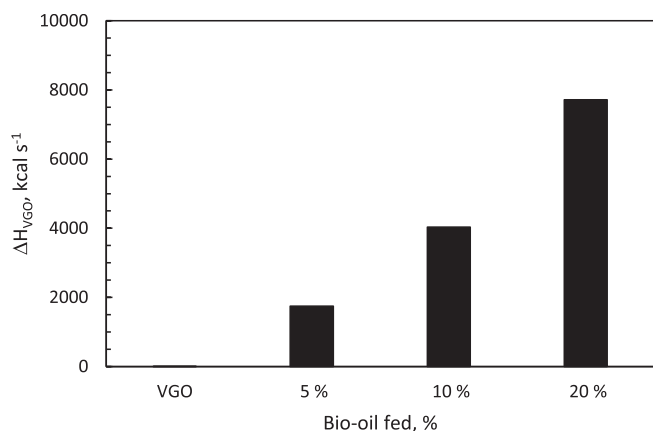


Fig. 6. Additional power required to preheat VGO from the temperature of the base case vs. percentage of bio-oil in the feed.

Table 14

Simulation results, maintaining the VGO preheating temperature constant at $223 \text{ }^\circ\text{C}$, for several C/O ratios. Feedstock 95 wt% VGO – 5 wt% bio-oil.

	C/O, $\text{kg}_{\text{cat}} \text{kg}_{\text{feedstock}}^{-1}$					
	6.87	7.28	7.76	8.25	9.87	11.48
Catalyst flow rate, kg s^{-1}	425	450	480	510	610	710
Coke yield, wt%	6.55	6.55	6.57	6.60	6.78	7.06
Regenerator air flow rate, kg s^{-1}	66.40	65.90	65.55	65.20	64.30	63.65
Regenerator temperature, $^\circ\text{C}$	708.1	697.7	686.7	676.9	650.9	632.0
O ₂ in flue gas (dry basis), %	5.1	5.1	5.1	5.1	5.1	5.1
Mixing point temperature, $^\circ\text{C}$	546.2	545.2	544.1	543.1	540.1	537.5
VGO preheating temperature, $^\circ\text{C}$	223	223	223	223	223	223

is fed to the mixture at $40 \text{ }^\circ\text{C}$.

The steady state operation of the unit under different C/O ratios was simulated at given contents of bio-oil in the mixture, calculating the yield of coke needed to maintain the VGO preheating temperature at $223 \text{ }^\circ\text{C}$ (reference temperature). By representing the curves of coke yield as a function of the C/O relationship calculated in the simulation for different bio-oil contents and the experimental information, the intersection point corresponds to the C/O ratio that will maintain the desired VGO preheating temperature unchanged.

Table 14 shows the results of the simulations for the case of co-processing 5 wt% bio-oil – 95 wt% VGO when the heat of cracking of dry bio-oil is the same as VGO, 140 kcal kg^{-1} , giving a mixture cracking heat of $134.8 \text{ kcal kg}^{-1}$. Fig. 7 shows the experimental yield of coke as a function of the C/O ratio for the 95 wt% VGO – 5 wt% bio-oil mixture. This figure also shows the coke yield required to keep at $223 \text{ }^\circ\text{C}$ (base case) the preheat temperature of the VGO when different C/O ratios are used. The calculated curves correspond to certain values of dry bio-oil cracking heat.

It can be seen in Fig. 7 that the coke yield (experimental information) increases almost linearly as the C/O ratio increases.

The intersections of the calculated coke yield curves with the coke yield-C/O line represent the C/O ratio that should be used in the FCC unit to maintain the VGO preheating temperature constant, depending on the heat of cracking of the mixture. The less endothermic the heat of cracking, the lower the C/O ratio required, results being extremely similar for all the scenarios.

In the case of the 90 wt% VGO – 10 wt% bio-oil mixture, the results of the simulation for the same heat of cracking are shown in Table 15

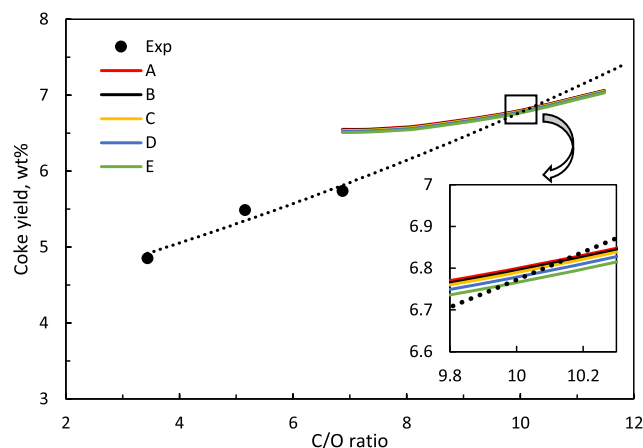


Fig. 7. Coke yields vs. C/O ratio for the 95 wt% VGO – 5 wt% bio-oil mixture. Points: experimental. Solid lines: computed for several heats of dry bio-oil cracking (kcal kg^{-1}): A, 140; B, 100; C, 60; D, 0; E, -80 .

Table 15

Simulation results, maintaining the VGO preheating temperature constant at 223 °C, for several C/O ratios. Feedstock 90 wt% VGO – 10 wt% bio-oil.

	C/O, kg _{cat} kg _{feedstock} ⁻¹				
	6.87	8.25	9.86	11.97	13.91
Catalyst flow rate, kg s ⁻¹	425	510	610	740	860
Coke yield, wt%	7.13	7.14	7.29	7.65	8.11
Regenerator air flow rate, kg s ⁻¹	72.60	71.08	69.95	68.95	68.40
Regenerator temperature, °C	719.4	686.3	658.8	633.8	617.2
O ₂ in flue gas (dry basis), %	5.1	5.1	5.1	5.1	5.1
Mixing point temperature, °C	544.7	541.8	538.8	535.7	533.3
VGO preheating temperature, °C	223	223	223	223	223

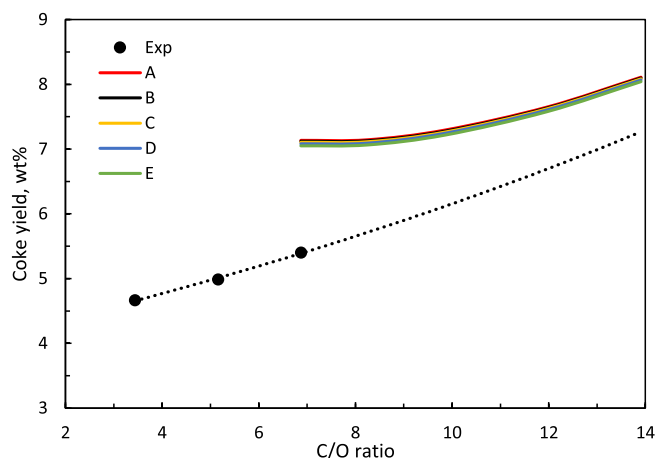


Fig. 8. Coke yields vs. C/O ratio for the 90 wt% VGO – 10 wt% bio-oil mixture. Points: experimental. Solid lines: computed for several heats of dry bio-oil cracking (kcal kg⁻¹): A, 140; B, 100; C, 60; D, 0; E, –80.

and Fig. 8.

Fig. 8 clearly shows that the coke yield is not enough to achieve a C/O ratio able to maintain the VGO preheating temperature in the FCC unit constant at 223 °C when a 90 wt% VGO – 10 wt% bio-oil mixture is co-processed.

5. Conclusions

The simulation of a FCC unit following typical operational procedures (constant C/O relationship, constant preheating temperature) allowed quantifying which is the effect of co-feeding the aqueous fraction of a bio-oil and a conventional VGO on the heat balance of the process. The heat provided by the regeneration of the catalyst and the energy requirements to preheat and vaporize the feedstock and sustain the endothermic cracking reactions were considered.

Laboratory experimental results gathered in a fluidized bed reactor showed high consistency in coke yields as a function of the content of bio-oil in the mixture at various C/O relationships.

The high content of water in the bio-oil limits the amount of aqueous bio-oil which can be added to the standard hydrocarbon feedstock to around 5 wt%, as the heat generated in the combustion of coke is not enough to sustain the energy demand of the whole FCC unit. In this sense, it has to be considered that the heat of coke combustion, when formed from the mixture, is lower than that from VGO alone.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

This work has been carried out with the financial support of the Ministry of Science, Innovation and Universities (MICIU) of the Spanish Government (grant RTI2018-096981-B-I00), the European Union's ERDF funds and Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie Actions (grant No 823745) and the Basque Government (grant IT1645-22). The financial support of the Universidad Nacional del Litoral (UNL, Santa Fe, Argentina), Proj. CAID 50420150100068LI, and Agencia Nacional de Promoción Científica y Tecnológica (ANPCyT), PICT 1208/2016 is gratefully acknowledged.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.fuel.2022.124798>.

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