

Different options to upgrade engine oils by gasification with steam and supercritical water



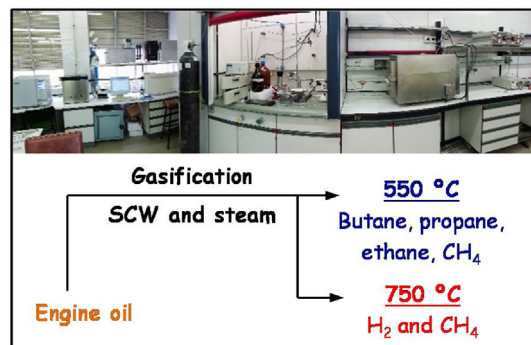
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HIGHLIGHTS

- Upgrading engine oils by gasification with steam and supercritical water up to 500 bar.
- Two different ways of upgrading are proposed depending on the temperature.
- This method achieves turn more than 85% of oil into valuable gases.
- The effect of pressure on gasification depends on the structure of feed-stock.

GRAPHICAL ABSTRACT



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ABSTRACT

This work reports for the first time a treatment to manage engine oils in an environmentally friendly manner which, besides, upgrades them into valuable gases: gasification with steam and supercritical water (SCW). Pressure, temperature and wt% ranges from 50 to 500 bar, 500–800 °C and 0.42–2.0%, respectively, were investigated. The process can be faced in two different ways regarding the temperature. A low-temperature gasification at 550 °C to transform up to 60% of oil into carbon-containing gases such as CH₄ and ethane in less than 2 min; and a high-temperature gasification at 750 °C that produces H₂, CH₄ and CO₂ as main gaseous products. Namely, SCW gasification at 250 bar, 750 °C and 0.83 wt% for 1.9 min transformed more than 85% of the oil into a gaseous mixture containing 37% H₂ and 29% CH₄, two valuable green fuels. The treatment is herein used to upgrade fresh engine oils but it is potentially applicable to the upgrading of such an abundant and polluting residue as waste engine oils.

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1. Introduction

Lube oils are complex blends of hydrocarbons generated in the refining process of crude oil. These oils must be periodically changed because the original hydrocarbons are progressively degraded, and water and charred residues are added to the blend during their lifetime; thus oils are unable to accomplish their original role. Currently, waste lube oils (WLOs) are the most abundant liquid pollutant in Europe [1]. Furthermore, WLOs are highly pollu-

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tant residues since they contain polycyclic aromatic hydrocarbons (PAHs) and high levels of heavy metals [2].

WLOs can be managed in different ways. The regeneration of WLOs is achieved through a series of treatments (removal of water and fuel added during its lifetime; removal of solid particles, such as heavy metals and soot; fractionating stage; and removal of chlorinated, oxygenated, and sulphurated species) that allows recovering and reusing a fraction of the original blend [3,4]. Regeneration leads to the greatest reduction of the environmental damage [5], but not all of the WLOs can be regenerated. It is estimated that only 60–65% of WLOs can be regenerated since they must fit specific polluting levels and viscosity indexes [3]. Furthermore, a highly polluting fraction is discarded during the regenerating process that demands further purification treatments.

Bioremediation is an alternative to regeneration, in which WLOs are degraded by the biological activity of certain microorganisms, usually bacteria [6,7]. The pollutants are destroyed, but the energetic potential contained in the blend is wasted. WLOs can also be reused without any treatment sometimes, e.g., as a lube in other applications [8] or as a binder in the manufacturing of asphalt and cements [9,10].

Different techniques exist that allow making the most of the energetic power contained in WLOs. Their use as fuels in cement kilns was the most employed valorization method until recent decades [2], but this method damages the environment because it releases significant amounts of polluting gases. Fractionating the hydrocarbons contained in the WLOs to transform them into valuable species is a trending alternative to direct burning [5]. Thermal cracking is the most classical method to crack hydrocarbons, and when followed by a distillation stage, allows obtaining short-chain hydrocarbons from WLOs [11]. Most of efforts concerning this technology are focused on the production of liquid diesel-like hydrocarbons [12,13]; however, depending on the process conditions, volatile hydrocarbons can be obtained [14,15]. Classical heating with hot inert gases is the starting point to other technologies, such as catalytic thermal cracking [16,17], pyrolytic distillation [18,19], electric-arc pyrolysis [20], or pyrolysis with microwave heating [21]. High-temperature oxidation is another alternative to upgrade WLOs. Guo et al. [22] made a partial oxidation of a mixture bio-oil/WLO with air at 1050–1100 °C to produce syngas; however, their ultimate goal was not gasifying the mixture but producing syngas as a reagent to synthesize lower alcohols (C₁–C₅ mixed alcohols).

On the other hand, gasification with steam is one of the most common methods to upgrade different types of biomass with an organic base. Gasification is likely to be an ideal and practical method for waste to energy application if the extremely high process temperature (up to 1600 °C), which is the main limitation of this technology, can be reduced to a lower process temperature [11]. When steam is compressed above the critical pressure of water ($P_c = 221$ bar), the resulting fluid shows different properties to steam. Supercritical water (SCW) dissolves organic compounds and gases, what reduces mass transfer limitations, and it also behaves as a reagent and a catalyst [23].

Steam and SCW have been used to gasify and upgrade different types of biomass and organic pollutants [24–28]. SCW gasifies the biomass more efficiently than steam given its above-commented properties; thus, supercritical gasification can be performed at lower temperatures than steam gasification. Although this method is widely spread to upgrade biomass, the gasification with steam and SCW of WLOs, a different type of organic residue, has not been explored to the best of our knowledge. For the first time, this study reports the gasification of engine lube oils with water under different states of the matter, steam and SCW, and their conversion into different valuable gases.

WLOs contain noticeable amounts of heavy metals and PAHs [29–31], highly harmful compounds for human health. The health risks that the performance of many gasification assays using WLOs may imply led us to perform the study using fresh synthetic lube oil, a blend with a similar composition but with low aromatic contents and without heavy metals. Linear and branched paraffins with high molecular weights are the main compounds contained in these blends, but they have also a meaningful cyclic paraffin content [32,33].

2. Experimental section

2.1. Materials

Fresh synthetic engine oil Repsol 5W40TDI was used in the gasification assays. The density of the oil was 0.84 g cm⁻³. The compounds contained in these kinds of oil are usually characterized with complex analytical techniques based on the simultaneous running of several chromatographic columns [32,33], but this technology was not available for us. The available GC–MS technology (described later) was not able to separate the contained compounds enough to precisely identify them, (see ESI section S1). The hydrocarbons contained in the oil were estimated to have more than 20 carbon atoms, but its exact composition could not be determined. However, its elemental composition could be determined by combustion at 1000 °C in a LECO CHNS-932 equipment: 84.77 wt% carbon, 13.48 wt% hydrogen, 0.26 wt% nitrogen and 0.22 wt% sulphur. Cyclohexane (purity of >99.8%) was purchased from Carlo Erba Reagents and used as received. Dodecane (purity of >99.8%) was purchased from Sigma-Aldrich and used as received. Water was purified with a Milli-Q device before its use.

2.2. Experimental procedure

2.2.1. Gasification

The experimental procedure was thoroughly described elsewhere [34]. In summary, a water stream pumped by a HPLC ChromTech pump went through a preheater before reaching the Hastelloy reactor. The tubular reactor consisted of a 17 cm³ internal volume spring-manufactured tube (4.1 m length x 1/4" OD x 0.080" wall). The reactor was situated inside of an electrical furnace and was heated to the reaction temperature. Once the reaction temperature had been attained, the oil was pumped by a HPLC LabAlliance Series 1500 pump and was mixed with the water preheated to the reaction temperature at the entrance of the reactor. The stream leaving the reactor was cooled to ambient temperature, went through a filter and was discharged through a pressure-regulating valve. A schematic of the installation can be found in the ESI, section S2.

Once the steady state had been attained, the process was maintained for 60 min to assess the stability of the reaction. After that period of time, the oil flow was stopped and the water flow was maintained for 30 min to remove any pollutant deposited on the reactor. The reaction time of each assay was calculated by approaching the density of the mixture to that of pure water at the same reaction pressure and temperature.

The pressure and temperature ranges analyzed spread from 50 to 500 bar, and from 500–800 °C, respectively. Pressures lower than 50 bar were not assayed because the corresponding reaction times were not long enough to be suitably compared to the reaction times achieved at higher pressures. wt% was defined as follows, Eq. (1):

$$wt (\%) = \left(\frac{\text{oil mass flow feeding}}{\text{oil mass flow feeding} + \text{water mass flow feeding}} \right) \times 100 \quad (1)$$

The wt% range investigated was from 0.42 to 2%. These wt% values correspond to oil:water ratios from 1:240 to 1:50. Lower ratios could not be experimented because the amounts of gas generated by greater oil flows could not be managed in the available installation.

2.2.2. Analysis of the produced gaseous stream

The flow, composition, and concentration of the produced gases were analyzed. The gaseous stream went through a few stages before its analysis: separation from the liquid stream in a gas-liquid separator, cooling to $-20\text{ }^{\circ}\text{C}$ to retain the remaining humidity, and heating to $30\text{ }^{\circ}\text{C}$. The concentrations of gases (vol%) were calculated combining the data obtained in (i) a Shimadzu GC-2010 Plus gas chromatograph with a H_2 flame ionization detector, and (ii) a GC-MS system consisting of a Teknokroma TR-GC1102010 chromatographic column and an Omnistar GSD 300 mass spectrometer. Further explanation about the analytical experimental procedure is detailed in ESI section S2. The analyzed gases were H_2 , CO , CO_2 , CH_4 , ethane, ethylene, acetylene (the sum of ethane, ethylene, and acetylene is shown as C_2), propane, propylene (the sum of propane and propylene is shown as C_3) and butane. The generated flow of gases was continuously measured in a Resteck Pro-Flow 6000 electronic flowmeter.

The gasification efficiency was evaluated from carbon gasification efficiency (CGE), Eq. (2), which could be calculated by characterizing the gaseous effluent:

$$\text{CGE} = \left(\frac{\text{carbon mol flow in the produced gas}}{\text{carbon mol flow in the oil feeding}} \right) \quad (2)$$

Gas Yield was defined as follows, Eq. (3):

$$\text{Gas Yield} = \left(\frac{m_{\text{produced gas}}}{m_{\text{feeding oil}}} \right) \quad (3)$$

Where $m_{\text{produced gas}}$ (g min^{-1}) is the mass flow of the produced gas and $m_{\text{feeding oil}}$ (g min^{-1}) the mass flow of oil feeding the reactor.

CGE and Gas Yield are not strictly comparable because of their different units but the comparison of their trends allows reaching conclusions about the extent of cracking and reforming reactions implied in gasification. A table with the results of CGE and Gas Yield for all the experiments can be found in the ESI, section S3.

Regarding the energy aspects of gasification, Energy Recovery was defined as follows, Eq. (4):

$$\text{Energy Recovery} = \frac{\text{Energy flow}_{\text{gas}}}{\text{Energy flow}_{\text{feeding oil}}} \quad (4)$$

Where $\text{Energy flow}_{\text{gas}}$ (kJ min^{-1}) and $\text{Energy flow}_{\text{feeding oil}}$ (kJ min^{-1}) are the energy flows of the gas stream produced and the feeding oil, respectively. Energy flow is calculated as the product of the Higher Heating Value (kJ kg^{-1}) and the mass flow (kg min^{-1}) of the corresponding stream.

Energy Efficiency was defined as follows, Eq. (5):

$$\text{Energy Efficiency} (\%) = \left(\frac{\text{Energy flow}_{\text{gas}}}{\text{Energy Input}} \right) \times 100 \quad (5)$$

Where Energy Input is an estimation of the amount of energy spent in the process (kJ min^{-1}).

Further information about the calculation of Energy Recovery and Energy Efficiency are described in ESI Section S4.

2.2.3. Analysis of the produced liquid stream

In each assay, a liquid sample was taken from the separator to subsequently analyze its composition. These samples were analyzed by gas chromatography with mass spectrometry (GC-MS) on an Agilent 7890a chromatograph equipped with an MS detector with an ionic trap Agilent MS220. A homogeneous $1\text{ }\mu\text{L}$ sample was

extracted with 1 mL of ethyl acetate. Then, $1\text{ }\mu\text{L}$ of the extract was injected in the chromatograph with a split ratio 20:1. An Agilent VF-5 chromatographic column was used, with a length of 30 m ; an internal diameter of 0.25 mm ; and a thick layer of $25\text{ }\mu\text{m}$, with 25 mL/min of He as the carrier gas. The injector was maintained at $270\text{ }^{\circ}\text{C}$, and the following temperature program was used in the oven: an initial temperature of $50\text{ }^{\circ}\text{C}$ maintained for 5 min , followed by heating at $10\text{ }^{\circ}\text{C/min}$ to $270\text{ }^{\circ}\text{C}$, which was finally maintained for 5 min . The detection mode was selected as electronic impact ionization. Masses from 50 to 500 u were recorded. The relative standard error of this technique was 10% .

3. Results and discussion

3.1. Obtained products

In addition to gases and compounds contained in the liquid effluent, the formation of a third type of product, a carbonized solid residue or char, was observed. Small char particles were retained in the filter placed before the pressure-regulating valve, but the installation used herein hindered quantifying the amounts of char formed under different reaction conditions.

GC-MS analysis determined that the main products contained in the liquid effluent were phenol and PAHs (naphthalene, phenanthrene, and pyrene). The areas of the peaks associated with PAHs were integrated in a unique area to make the interpretation of the results easier. The analysis of the produced gases also revealed the presence of phenol, indicating that phenol was distributed between the liquid and gaseous effluents. The amount of phenol contained in the gaseous effluent was analysed from the area of the peak that this species generated in the chromatographic analysis. The areas of the peak associated with phenol contained in the gas were small compared with the remaining species detected in the chromatograph (see ESI section S5). Due to its low concentrations in the gas, phenol was not included in the calculation of the concentrations of the species contained in the gaseous effluent or in the calculation of CGE. Other compounds detected in the GC-MS analysis of the liquid samples were xylenes, dymethylbenzene and trimethylbenzene, but their concentrations were negligible compared to those of PAHs and phenol (see ESI section S6). The presence of tetrachloroethylene was also detected in all of the samples (retention time in column: 5.1 min). This compound also appeared in the chromatogram of the original oil (see ESI section S1). It was concluded to be an additive of the oil that the method did not degrade under the assayed conditions.

3.2. Effect of temperature

Regarding the lack of research about lube oil gasification with steam and SCW, it was first tested whether the method was able to transform the oil into gaseous carbon-containing products and H_2 .

Temperature seemed to be one the parameters that most significantly governed the process [35], so that the research was began with the study of the effect of this parameter on gasification at 50 bar . Fig. 1a shows how CGE and Gas Yield varied in this study. The oil began to be gasified at $500\text{ }^{\circ}\text{C}$; the production of gas was negligible at lower temperatures. CGE increased as the gasification temperature rose. Gasification generated a mixture of gaseous products at concentrations that varied with the reaction temperature. Fig. 1b and 1c show the influence of temperature on the concentrations of the species contained in the gas.

Butane, C_3 and C_2 concentrations behaved similarly; they slightly decreased when heating from 500 to $550\text{ }^{\circ}\text{C}$ and then rapidly decreased to zero over that temperature. The heavier hydrocarbons were less concentrated in the mixture and disappeared at

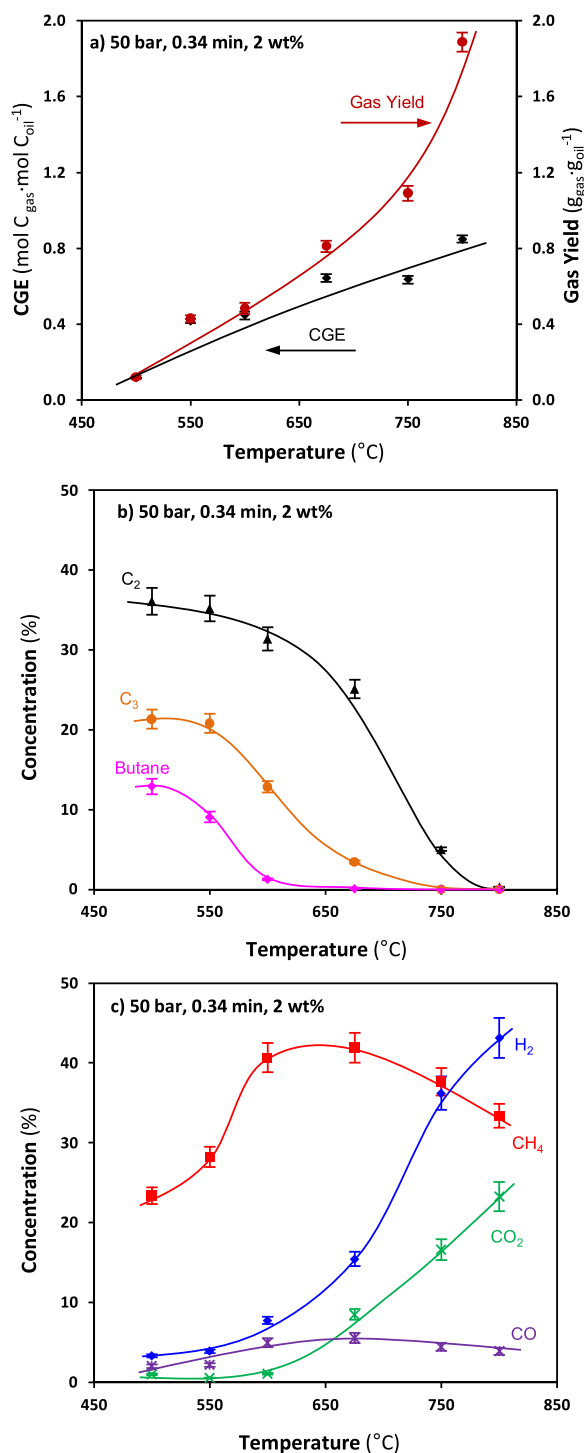


Fig. 1. Effect of temperature at 50 bar, 0.34 min and 2 wt% on (a) CGE and Gas Yield; the concentrations of the species contained in the gaseous effluent (b) butane, C₃ and C₂, and (c) CH₄, CO, CO₂ and H₂.

lower temperatures. CH₄ already appeared at 500 °C, and its concentration increased up to 575 °C, plateaued, and began to slightly decrease at temperatures greater than 675 °C. CO concentration remained low (2–6%) and minimally changed throughout the range of temperatures. The CO₂ registered below 600 °C was negligible; above this temperature, its concentration constantly increased as the temperature increased. The trend for H₂ was similar to that of CO₂; however, in this case, a concentration of 3% was already registered at 500 °C. The increase in concentration with temperature

was also greater, thus reaching a 43% concentration at 800 °C compared with 23% for CO₂. This study confirmed that the method was able to gasify the engine oil and transform it into valuable gaseous products.

At temperatures lower than 600 °C, the gaseous product was essentially formed by butane, C₃, C₂ and CH₄. The cracking of the compounds contained in the fed oil to generate short-chain hydrocarbons was the predominant reaction in the system [34]. On the other hand, at the highest temperatures investigated, 750 and 800 °C, two valuable carbon-containing gas remained in the mixture CH₄ and CO, although CH₄ concentration, about 34%, was higher than CO concentration, 4%. Furthermore, high concentrations of another valuable gas, H₂, were registered. The decrease in C₃ and C₂ concentrations suggested that, under these conditions, these hydrocarbons were probably being reformed by water to produce H₂ and other by-products, what agrees with the increase in H₂ concentration. Gas Yield is another parameter whose behaviour reveals the relevance of reforming reactions. At temperatures below 600 °C CGE and Gas Yield essentially coincided, probably because the reforming reactions reached low conversions. However, above 600 °C water seemed to play a relevant role not only as reaction medium but also as a reagent. As a consequence of the great amounts of H₂ produced in these high-temperature reforming reactions, Gas Yield already reached higher values than CGE at 675 °C (0.81 and 0.64, respectively), and this difference was boosted as reaction temperature rose. At 800 °C, Gas Yield value was near to 2 and was the double of CGE value, what showed that an important fraction of the products mass came from water.

Consequently, Fig. 1b and 1c showed that the gasification method provided two upgrading options: low-temperature gasification to produce carbon-containing gases and high-temperature gasification to produce CH₄ and H₂.

3.3. Low-temperature gasification: production of valuable carbon-containing gases

Fig. 2a shows the effect of reaction time and pressure on oil gasification at 550 °C.

CGE rapidly increased at the beginning of the process for the lowest pressures investigated, 50 and 150 bar, but already trend to steadiness for short reaction times. The available installation did not allow exploring longer reaction times for these low pressures. 250 bar gasification slope was smaller but CGE only trended to steadiness at longer reaction times compared with steam gasification. At 350 bar the slope was even less marked, and the curve also seemed to describe a plateau when increasing the reaction time. CGE was observed to decrease with pressure within the supercritical region. As a result of the effect of both parameters in gasification, the highest CGE reached in this study was 0.59 for gasification at 550 °C and 250 bar during 1.89 min. That is to say, about 60% of the oil was transformed into gas.

The amount of PAHs contained in the liquid effluent and the phenol contained in the liquid and gaseous effluents were analysed. Fig. 2b shows how PAHs in the liquid effluent evolved for 550 °C gasification. At the earliest seconds of gasification, the amount of generated PAHs essentially increased in a linear trend, and this increase was more pronounced for the highest pressures assayed. Beyond 0.6 min, an evident decrease in PAHs content was observed for supercritical gasification.

Fig. 2c shows the evolution of phenol contained in the gaseous effluent. Herein, a clear effect of pressure was not observed for the shortest reaction times. However, as gasification was lengthened, the greater production of phenol related to high pressures became evident. Phenol in the liquid effluent showed similar trends than those observed in Fig. 2c.

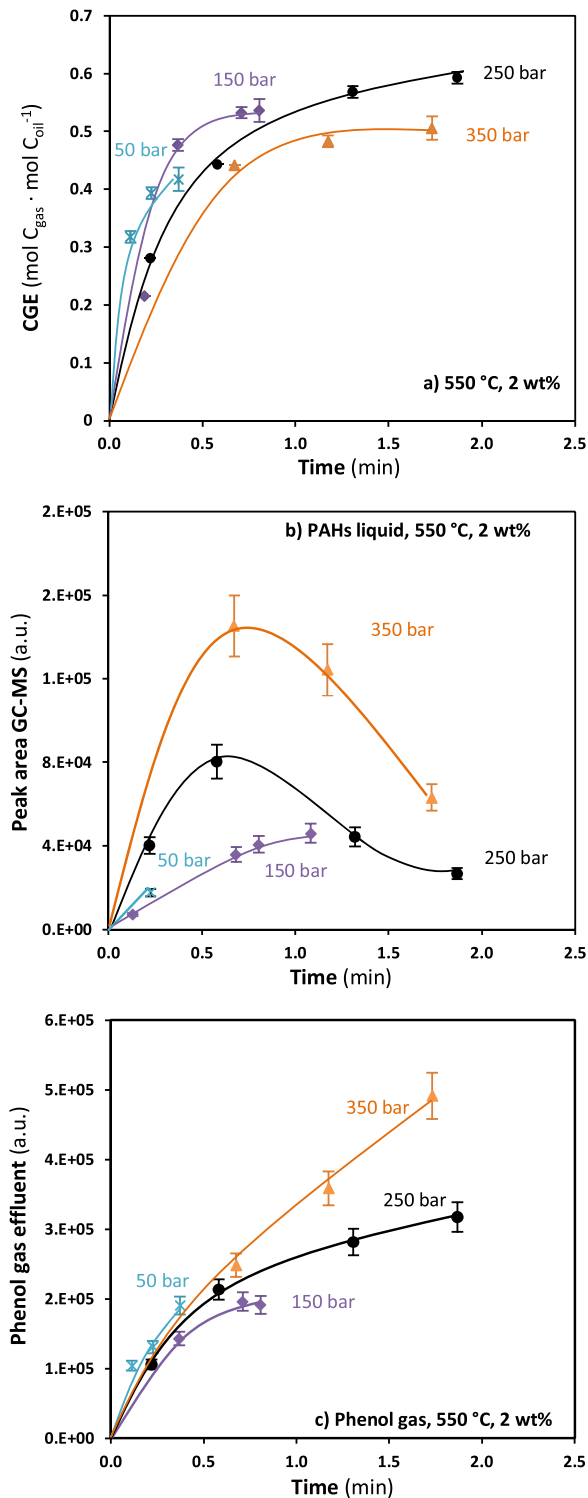


Fig. 2. Effect of reaction time and pressure on (a) CGE, (b) the production of PAHs and (c) the production of phenol, for gasification at 550 °C and 2 wt%.

In other works, the formation of significant amounts of phenol was probed to limit the gasification of linear hydrocarbons [34]. Then, both the increase in PAHs and phenol generation with pressure may be related to the previously commented decrease in CGE with pressure (Fig. 2a). A more detailed analysis of the effect of pressure on gasification is reported in the following section.

The analysis of the concentrations of the species contained in the gaseous mixture revealed further information, Table 1. First, it was

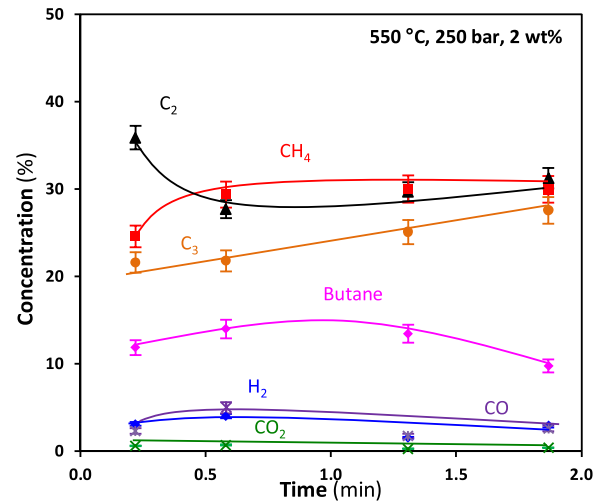


Fig. 3. Effect of reaction time on the concentrations of the species produced for gasification at 550 °C, 250 bar and 2 wt%.

confirmed that low-temperature gasification essentially produced the valuable carbon-containing gases butane, C₃, C₂ and CH₄; H₂, CO and CO₂ concentrations were less than 5% for all the investigated pressures. Due to the low H₂ concentrations registered, CGE and Gas Yield essentially agreed. Because of this similarity only CGE was represented in Fig. 2a, but Gas Yield values for these reaction conditions can be found in ESI.

Pressure did not significantly affect these concentrations. Table 1, which reports the gases concentrations for gasification assays performed at different pressures but comparable reaction times, confirms this statement.

The effect of time on gas concentration for low-temperature gasification at 250 bar is shown in Fig. 3. When the reaction time was lengthened from 0.20 to 1.9 min, the concentrations of butane and C₂ decreased from 14.0 ± 0.8 and 35.9 ± 1.3%, to 9.9 ± 0.7 and 31.2 ± 1.1%, respectively; whereas the concentrations of C₃ and CH₄ increased from 21.4 ± 1.2 and 24.4 ± 1.2% to 27.6 ± 1.4 and 30.0 ± 1.4%, respectively. Thus, the gasification of this engine oil at 250 bar and 550 °C during 1.9 min produced 0.08 g_{CH4} g_{oil}⁻¹, 0.18 g_{C3} g_{oil}⁻¹, 0.23 g_{C2} g_{oil}⁻¹ and 0.11 g_{butane} g_{oil}⁻¹. That is to say, 0.60 g of these valuable carbon-containing gases were produced per gram of treated oil.

In other works, some hydrocarbons, namely, n-hexadecane and polyethylene, were exposed to both classical pyrolysis and hydrothermal cracking [36], and different results were obtained depending on the treated compound. When n-hexadecane was exposed to both treatments, no difference was observed between them; it was concluded that the chemistry of the process was largely thermal, and the role of SCW was not essential in the chemical conversions [37]. However, differences between the two treatments were observed for polyethylene. These differences were attributed to the different reactive phases [36]: Pyrolysis mainly occurred in a molten phase, whereas SCW could dissolve some hydrocarbons produced. Similar conclusions could be obtained for our study. It could be thought that the chemistry of the process was essentially thermal, but the data suggested that greater amounts of gaseous products were generated in the presence of water. This finding highlights that water plays a key role in the process, hydrolysing the contained compounds and improving their cracking in relation to classical pyrolysis.

This new upgrading procedure for lube oils has a few advantages regarding existing methods. Removing the humidity contained in the WLO is not necessary as in classical thermal cracking. Furthermore, and despite using a lower temperature, the production of

Table 1
Gas concentrations for 550 °C gasification at 2 wt% and different pressures.

Pressure (bar)	Reaction time (min)	Gas concentration (%)						
		H ₂	CO	CO ₂	CH ₄	C ₂	C ₃	Butane
150	0.68	4.0 ± 0.3	2.7 ± 0.3	0.9 ± 0.1	28.7 ± 1.4	31.5 ± 1.2	21.0 ± 1.2	11.2 ± 0.8
250	0.58	4.0 ± 0.3	5.0 ± 0.5	0.6 ± 0.1	29.0 ± 1.5	27.9 ± 1.0	19.5 ± 1.1	14.0 ± 1.0
350	0.67	3.9 ± 0.2	3.2 ± 0.4	0.7 ± 0.1	28.0 ± 1.3	30.1 ± 1.1	22.2 ± 1.2	11.9 ± 0.9

valuable gases is greater than for other methods. On the other hand, the technique has low selectivity; the reaction time and temperature must be chosen in detail, and the characteristics of the raw material must be well weighed to achieve the aim products and not others [38]. Furthermore, under the conditions assayed herein, 50–60% oil was gasified. This finding implied that a meaningful fraction of the residue was not upgraded and transformed into the desired products.

3.4. High-temperature gasification: production of CH₄ and H₂

Fig. 1 shows that high-temperature gasification is an interesting option in spite of its energy requirements since great amounts of oil are gasified and two valuable gases, CH₄ and H₂, are obtained as main products together with CO₂. High-temperature gasification study first analysed the influence of pressure to assess the optimal upgrading conditions. Fig. 4a shows the effect of pressure on CGE and Gas Yield for oil gasification at 750 °C during 0.31 min.

The amounts of gasified oil were greater than those at low-temperature gasification. For example, CGE for low-temperature gasification at 150 bar for 0.37 min was 0.48, whereas at high-temperature gasification at 150 bar for 0.30 min CGE increased up to 0.66.

Regarding the effect of pressure, CGE remained unchanged from 50 to 150 bar and beyond this pressure, it slightly decreased while compressing the fluid within the supercritical region. Lube oil was a complex blend of hydrocarbons in which linear paraffins predominated. In a previous work, the gasification of the linear paraffin dodecane was probed to slow down as pressure increased in the whole pressure range investigated, from 1 to 500 bar [34]. This phenomenon was confirmed for the pressure range investigated herein, 50 to 500 bar, by making a new study about dodecane gasification under the same conditions used for the oil (Fig. 4b). However, the slowing down for oil gasification was only observed above 150 bar and was not as marked as noted for dodecane. At this point it can be stated that the studies treating model compounds provide a suitable understanding of the chemical process, but they cannot predict how the presence of compounds with different structures in a heterogeneous organic feedstock may affect the process [39]. Namely, this type of oil contains a meaningful percentage of cyclic paraffins and a small PAHs content. In another work, it was found that the gasification of phenol accelerated when the pressure increased over the whole pressure range investigated (1–1000 bar) [40]. To date and as far as we know, no work has explored the effect of pressure on the gasification of cyclic paraffins. Consequently, CGE for the gasification of a model cyclic paraffin, cyclohexane, was also investigated (Fig. 4c).

Two different reaction conditions were investigated, and the same conclusion was reached for both of conditions. The amounts of gasified cyclohexane did not depend on the gasification pressure. The explanation for this phenomenon was not within the objectives of this research, but this series of results allowed reaching a new conclusion applicable to the overall field of gasification with steam and SCW. Namely, the effect of pressure on gasification depends on the structure of the compound to gasify. As a result, it is probable that the effect of pressure on the gasification of a blend is a synergy of the effects of pressure on the gasification of its individ-

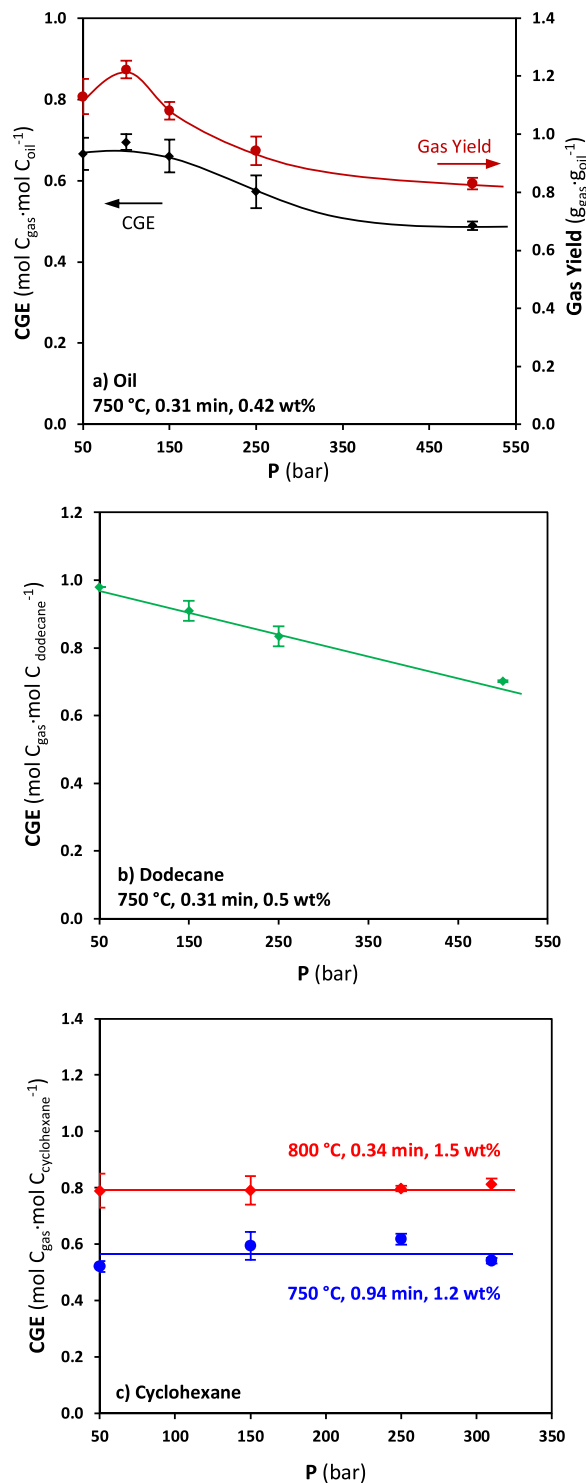


Fig. 4. (a) Effect of pressure on CGE and Gas Yield for gasification of the oil at 750 °C, 0.31 min and 0.42 wt%; effect of pressure on CGE for gasification of (b) dodecane at 750 °C, 0.31 min and 0.5 wt% and (c) cyclohexane at 750 °C, 0.94 min and 1.2 wt% and 800 °C, 0.34 min and 1.5 wt%.

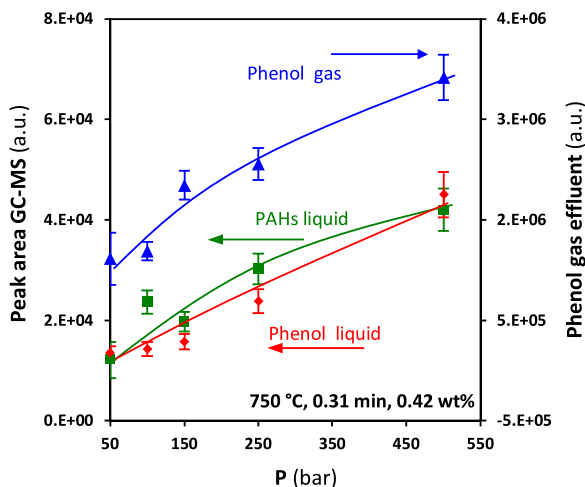


Fig. 5. Effect of pressure on the production of PAHs and phenol for gasification at 750 °C, 0.31 min and 0.42 wt%.

ual compounds. In our study, pressure affected the gasification of the individual compounds that formed the blend in different ways; it slowed down the gasification of linear paraffins, accelerated the gasification of PAHs, and had no influence on the gasification of cyclic paraffins. The presence of cyclic paraffins and PAHs in the blend softened the characteristic trend of linear paraffins. As a consequence, the slowing down of gasification was only observed for pressures above 150 bar and was not as marked as for dodecane. Thus, the optimal gasification pressure for blends with high linear paraffin contents, such as diesel, will be low (steam region), whereas the optimal gasification pressure for blends with high aromatic contents, such as bitumen, will be high (supercritical region).

Fig. 5, which shows the amounts of PAHs and phenol generated in high-temperature gasification of the oil, clarifies why the gasification slowed down at high pressure. Small amounts of PAHs and phenol were produced at 50 bar gasification, but greater amounts of these compounds were formed as the gasifying fluid was compressed. The highest phenol and PAHs concentrations were registered at the highest pressure assayed. When an organic molecule is contained in the bulk of SCW, the supercritical fluid can behave as a solvent or a reaction medium, reagent or even catalyst. Some of the reactions that organic molecules undergo when they are dissolved in SCW are condensation, coupling or cyclization reactions [37,41]. During oil gasification, linear paraffins with high molecular weights were cracked, and other short-chain paraffins were produced that could behave as reagents for cyclization or condensation reactions before being reformed to CO, CO₂ and H₂ [28,34]. In the gasification of the engine oil, these reactions produced PAHs and phenol, compounds that have been identified as the main hurdle for gasifying other organic feedstocks. Phenol is rather inert, and it hinders complete gasification because its degradation is difficult [25]. PAHs are not as difficult to degrade as phenol, but they are precursors for the formation of char [42,43]. Fig. 5 reveals that these reactions were more relevant at high pressures, explaining the lower CGEs achieved for these conditions.

The comparison of Figs. 2b and 5 reveals that the amounts of PAHs and phenol produced for gasification at 750 °C were greater than at 550 °C. In fact, the polymerization of liquid intermediates to cross-linked large molecules is a process that mostly occurs under high-temperature conditions [44]. This phenomenon was undesirable and problematic from a technical point of view since the presence of these compounds implied char formation. The formation of char and the waste of energy related to the use of high temperature and pressure were the main disadvantages of this upgrading method.

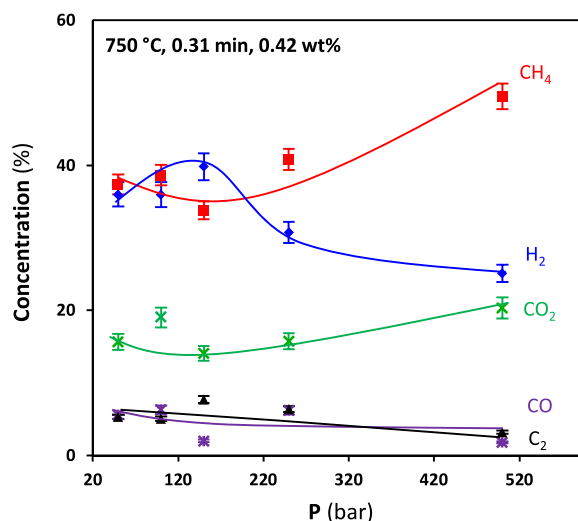


Fig. 6. Effect of pressure on the concentrations of the gaseous species produced for gasification at 750 °C, 0.31 min and 0.42 wt%.

As expected, the produced gaseous mixture contained CH₄ and H₂ as the main species (Fig. 6). H₂ was one of the final products from the global reaction and was generated on the reforming reaction of hydrocarbons and the water-gas shift reaction [34]. Thus, it exhibited a similar trend to CGE (Fig. 4a). A maximal 40% concentration was reached for one of the pressures at which the highest percentage of oil was gasified, 150 bar. As a result of the high yields that reforming reactions seemed to reach under this high-temperature conditions, Gas Yield was greater than CGE throughout the whole pressure range investigated, Fig. 4a. CH₄ concentration slightly decreased when compressing steam from 50 to 150 bar. Afterwards, it increased with pressure throughout the supercritical region; 50% concentration was reached at 500 bar. The interpretation of this trend is not easy. CH₄ was an intermediate compound in a mechanism with several consecutive individual reactions [34], and the global reaction was in a different stage for each pressure investigated. However, it was clear that the lowest conversions reached by reforming reactions was related with the highest CH₄ concentrations (minimum Gas Yield and H₂ concentrations while maximum CH₄ concentrations at 500 bar), and vice versa. CO₂ was the third most abundant species with concentrations of 15–20%; CO and C₂ concentrations were between 2–7%.

SCW gasified lower proportions of oil than steam for a specific reaction time, but this did not mean that steam was able to produce more H₂ and CH₄ than the supercritical fluid. The reaction times that supercritical gasification could attain inside a reactor were longer than those attained by steam given the high density of the supercritical fluid. For example, the reaction time was almost doubled when compressing from 150 bar ($\rho_{150 \text{ bar}, 750^\circ\text{C}} = 0.033 \text{ g cm}^{-3}$) to 250 bar ($\rho_{250 \text{ bar}, 750^\circ\text{C}} = 0.056 \text{ g cm}^{-3}$). The slow supercritical gasification kinetics were compensated by their long reaction times in such a way that the produced amounts of H₂ and CH₄ could be greater than in steam gasification. Thus, a pressure of 250 bar was chosen to assess the real ability of high-temperature gasification to upgrade the oil. Fig. 7a shows the effect of time on CGE and Gas Yield for oil gasification at 250 bar and 750 °C. Gasification was fast at the earliest moments; greater than a half of the oil was already gasified in slightly less than 8 s. At this reaction time, the gasification was in an intermediate stage. Butane and C₃ had already disappeared (Fig. 7b), but another intermediate product, CH₄, predominated in a gaseous mixture that also contained meaningful concentrations of C₂. CO and CO₂ concentrations were low and the differences between CGE and Gas Yield were not great, thus indicat-

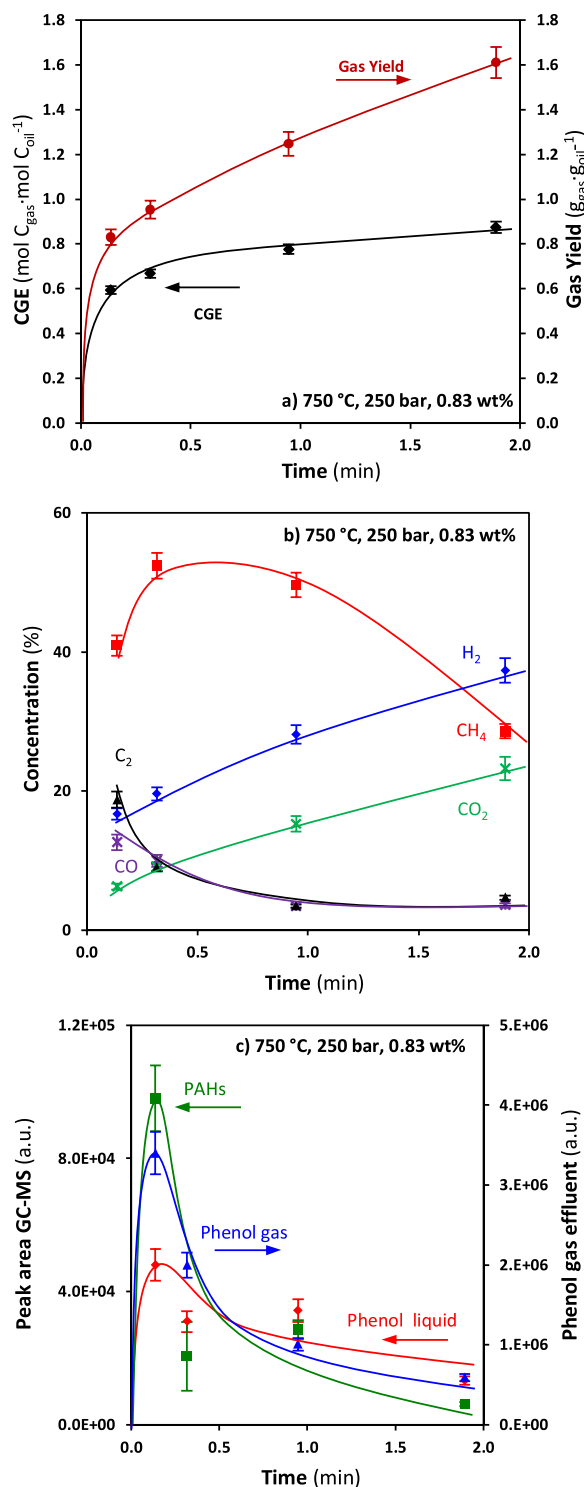


Fig. 7. Effect of time on (a) CGE and Gas Yield, (b) the concentrations of the gaseous species produced and (c) the production of PAHs and phenol, for gasification at 750 °C, 250 bar and 0.83 wt%.

ing that the reforming reactions had not reached great conversions yet. Gasification progressively slowed down as the reaction time was lengthened as shown by the decreasing of the slope of CGE. After 0.95 min of reaction, approximately 75% oil had been already gasified. C_2 had essentially disappeared, and the concentrations of the products from reforming reactions began to increase significantly. For the longest reaction time assayed (1.9 min), greater than 85% oil was gasified, and a gaseous mixture essentially formed by H_2

(37%), CH_4 (29%), and CO_2 (23%) was produced. On the other hand, and despite the observed slowing down in the gasification of the oil, Gas Yield steadily kept rising even for the longest reaction times investigated. That behaviour agrees with the increasing H_2 and CO_2 concentrations and the decreasing CH_4 concentration in Fig. 7b, and revealed that the reforming reactions were not complete.

Gas Yield value after 1.89 min was $1.61 \text{ g}_{\text{gas}} \text{ g}_{\text{oil}}^{-1}$, again reflecting the importance of reforming reactions in the production of gaseous products for this high-temperature gasification.

Regarding the products from the condensation and cyclization reactions, the high pressure and temperature conditions chosen for this study caused the formation of considerable amounts of PAHs and phenol at the earliest moments (Fig. 7c). Namely, PAHs generation was approximately 25% greater and the amount of phenol was 10 times greater compared with low-temperature gasification. However, SCW at 750 °C degraded these compounds after being formed. Their concentrations in the liquid and gaseous effluents rapidly decreased as the reaction time increased. They disappeared almost completely after 1.9 min; thus, at the end of this high-temperature reaction, less cyclization and condensation products remained in the liquid than in the low-temperature reaction. The disappearance of carbon-containing compounds from the liquid effluent agreed with the closeness to complete gasification observed for this reaction time in Fig. 7a. Consequently, if long enough reaction times were used, the above-commented problem caused by the formation of char could be solved.

In summary, this method allowed the transformation of almost all of the engine oil into gases without generating other by-products. The gaseous mixture contained CO_2 and two valuable gases considered as green fuels, H_2 and CH_4 . Specifically, $0.06 \text{ g}_{\text{H}_2} \text{ g}_{\text{oil}}^{-1}$ and $0.39 \text{ g}_{\text{CH}_4} \text{ g}_{\text{oil}}^{-1}$ were generated in the gasification of the oil at 250 bar and 750 °C during 1.9 min.

Some considerations can be made about energy aspects of the process. Table 2 shows that the gasification of the oil at 750 °C, 250 bar and 0.83 wt% during 1.89 min recovered 91% of the energy contained in the oil as a valuable mixture of gases. Gasification at 550 °C and 2.0 wt% recovered 68% of that energy under comparable conditions of pressure and reaction time.

This improvement is the result of the gasification of greater amounts of oil and the greater conversions reached by the reforming reactions, as shown by the trends of CGE and Gas Yield in Fig. 7a. However, this better performance is achieved at the expense of spending greater amounts of energy to heat the reacting blend up to higher temperatures. An estimated calculation of the amounts of energy required to carry out the upgrading at 550 and 750 °C allows comparing the Energy Efficiencies of the two gasification alternatives reported herein. The Energy Efficiency of low-temperature gasification was about two fold greater than at high temperature, but it must be noted that the oil mass flow treated in that assay was three fold greater than at 750 °C. In case the oil mass flow treated at 750 °C would have been the same that at 550 °C (this assay could not be carried out in the available installation because of the great gas flows produced), the Energy flow_{gas} would have been about three fold greater, and so would have been its Energy Efficiency, whereas the Energy input would barely vary. That suggests that under strictly comparable time, pressure and wt% conditions, high-temperature gasification would probably get greater Energy Efficiencies regarding low-temperature gasification. Thermodynamic and physical properties of SCW play an important role in this issue. Heating one water mol from 1 bar and 25 °C, to 250 bar and 550 °C takes $60.16 \text{ kJ mol}^{-1}$ (see ESI section S4), whereas heating it up from 550 °C to 750 °C only takes $10.30 \text{ kJ mol}^{-1}$ more. Furthermore, greater amounts of blend must be heated up at 550 °C than at 750 °C to achieve the same reaction times because of the higher density at 550 °C. These changes in water properties are the main factors explaining the better energy

Table 2

Energy evaluation of low- and high-temperature gasification under comparable conditions of pressure and reaction time.

T (°C)	P (bar)	t (min)	Experimental conditions			Energy indicators	
			Water mass flow (g min ⁻¹)	Oil mass flow (g min ⁻¹)	Water density (mg cm ⁻³)	Energy Recovery (kJ kJ ⁻¹)	Energy Efficiency (%)
550	250	1.87	0.70	0.014	78.52	0.68	20.06
750	250	1.89	0.50	0.004	56.17	0.91	11.04

performance of high-temperature gasification under these specific reaction conditions.

Several future prospects arise from the conclusions obtained in this work. The method must be confirmed to be able to efficiently upgrade WLOs; great difficulties are not expected given the similar composition to fresh lube oils studied herein. Reaching reaction conditions (higher temperatures, bigger reactors) that allow completely gasifying a WLO and exclusively transforming it into H₂ and CO₂ (complete reforming) and reaching higher Energy Recoveries and Efficiencies will be the ultimate challenge. In that case, the problems related to the formation of char and the presence of polluting by-products in the liquid effluent would disappear, the selectivity of the method would be improved, and the separation of the produced gaseous effluent downstream would be easier. In summary, the process would allow the transformation the polluting and abundant residue WLOs into a valuable green-fuel, H₂. All these questions will be addressed in future works.

4. Conclusions

This work reports the upgrading of fresh engine lube oils by gasification with steam and SCW in a pressure range from 50 to 500 bar. The study of the effect of temperature on gasification revealed that upgrading could be faced in two different ways depending on reaction temperature. The so-called “low-temperature gasification” was performed at 550 °C and generated valuable carbon-containing gases, such as propane, ethane or CH₄, as products. In the gasification at 550 °C under optimal conditions (250 bar, reaction time 1.9 min and 2 wt%), approximately 60% of the oil was gasified, and 0.08 g_{CH₄} g_{oil}⁻¹, 0.18 g_{C₃} g_{oil}⁻¹, 0.23 g_{C₂} g_{oil}⁻¹ and 0.11 g_{C₄} g_{oil}⁻¹ were produced. The so-called “high-temperature gasification” was performed at 750 °C and generated H₂ and CH₄ as main products. The study of the effect of pressure revealed an important novelty for the field of gasification of organic feedstocks with water. Namely, the effect of pressure on gasification depends on the structure of the compound to be gasified. Thus, it is probable that the effect of this parameter on the gasification of a blend is a synergy of the effects of pressure on the gasification of the individual compounds that form it. From a practical point of view, gasification at 750 °C under optimal conditions (250 bar, reaction time 1.9 min and 0.83 wt%) gasified greater than 85% of the oil and produced 0.06 g_{H₂} g_{oil}⁻¹ and 0.39 g_{CH₄} g_{oil}⁻¹. Gasification with SCW seemed to be the most effective upgrading method of engine oils among the few reported to date.

Declaration of Competing Interest

There are no conflicts to declare.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:<https://doi.org/10.1016/j.supflu.2020.104912>.

References

- [1] C.T. Pinheiro, V.R. Ascensao, C.M. Cardoso, M.J. Quina, L.M. Gando-Ferreira, An overview of waste lubricant oil management system: physicochemical characterization contribution for its improvement, *J. Clean. Prod.* 150 (2017) 301–308, <http://dx.doi.org/10.1016/j.jclepro.2017.03.024>.
- [2] R. Vazquez-Duhalt, Environmental impact of used motor oil, *Sci. Total Environ.* 79 (1989) 1–23, [http://dx.doi.org/10.1016/0048-9697\(89\)90049-1](http://dx.doi.org/10.1016/0048-9697(89)90049-1).
- [3] Y.L. Hsu, C.C. Liu, Evaluation and selection of regeneration of waste lubricating oil technology, *Environ. Monit. Assess.* 176 (2011) 197–212, <http://dx.doi.org/10.1007/s10661-010-1576-3>.
- [4] M. Shakirullah, I. Ahmad, M. Saeed, M. Arsalan-Khan, H. Rehman, M. Ishaq, A. Ali, Environmentally friendly recovery and characterization of oil from used engine lubricants, *J. Chin. Chem. Soc.* 53 (2006) 335–342, <http://dx.doi.org/10.1002/jccs.200600042>.
- [5] IFEU (Institut für Energie- und Umweltforschung Heidelberg), Updating the study, Ecological and Energetic Assessment of Re-refining Waste Oils to Base Oils, Substitution of Primarily Produced Base Oils Including Semi-Synthetic and Synthetic Compounds, 2017.
- [6] B. Ramesh, S. Sasi, K. Rarayanan, N. Vadivel, Treatment of engine oil effluent by electrooxidation and aerobic biological degradation, *Sustain. Environ. Res.* 21 (2011) 109–116.
- [7] L.B. Salam, Metabolism of waste engine oil by *Pseudomonas* species, *3 Biotech* 6 (2016) 98–108, <http://dx.doi.org/10.1007/s13205-016-0419-5>.
- [8] A. Ishibashi, Y. Sunagawa, K. Sonoda, S. Ezo, Performance of used engine oil as gear-cutting oil, *Tribol. Trans.* 47 (2004) 272–279, <http://dx.doi.org/10.1080/05698190490439292>.
- [9] X. Jia, B. Huang, J.A. Moore, S. Zhao, Influence of waste engine oil on asphalt mixtures containing reclaimed asphalt pavement, *J. Mater. Civ. Eng.* 27 (2015), 04015042-1–04015042-9.
- [10] H.M. Nadeem, N.Z. Habib, N.C. Aun, S.E. Zoorob, Z. Mustafa, R. Mesney, S. Suubita, Used engine oil as alternative binder for buildings—a comparative study, *Waste Resour. Manag.* 170 (2017) 57–65, <http://dx.doi.org/10.1680/jwarm.17.00005>.
- [11] S.S. Lam, R.K. Liew, A. Jusoh, C.T. Chong, F.N. Ani, H.A. Chase, Progress in waste oil to sustainable energy, with emphasis on pyrolysis techniques, *Renew. Sust. Energ. Rev.* 53 (2016) 741–753, <http://dx.doi.org/10.1016/j.rser.2015.09.005>.
- [12] A. Sinag, S. Güllbay, B. Uskan, S. Ucar, S.B. Özgürler, Production and characterization of pyrolytic oils by pyrolysis of waste machinery oil, *J. Hazard. Mater.* 173 (2010) 420–426, <http://dx.doi.org/10.1016/j.jhazmat.2009.08.100>.
- [13] A. Jonusas, L. Miknius, Influence of the process conditions on yield, composition, and properties of the products derived from the thermolysis of scrap tire and used engine oils blends, *Energy Fuels* 29 (2015) 6978–6987, <http://dx.doi.org/10.1021/acs.energyfuels.5b01540>.
- [14] R. Moliner, M.J. Lázaro, I. Suelves, Valorization of lube oil waste by pyrolysis, *Energy Fuels* 11 (1997) 1165–1170, <http://dx.doi.org/10.1021/ef970025s>.
- [15] C. Nerin, C. Domeño, R. Moliner, M.J. Lázaro, I. Suelves, J. Valderrama, Behaviour of different industrial waste oils in a pyrolysis process: metals distribution and valuable products, *J. Anal. Appl. Pyrol.* 55 (2000) 171–183, [http://dx.doi.org/10.1016/S0165-2370\(99\)00097-2](http://dx.doi.org/10.1016/S0165-2370(99)00097-2).
- [16] D.C. Vargas, M.B. Álvarez, A. Hidrobo, K.M. Van Geem, D. Almeida, Kinetic study of the thermal and catalytic cracking of waste motor oil to diesel-like fuels, *Energy Fuels* 30 (2016) 9712–9720, <http://dx.doi.org/10.1021/acs.energyfuels.6b01868>.
- [17] D. Lesmana, H.S. Wu, Pyrolysis of waste oil in the presence of a spent catalyst, *J. Environ. Chem. Eng.* 3 (2015) 2522–2527, <http://dx.doi.org/10.1016/j.jece.2015.09.019>.
- [18] R. Maceiras, V. Alfonsín, F.J. Morales, Recycling of waste engine oil for diesel production, *Waste Manage.* 60 (2017) 351–356, <http://dx.doi.org/10.1016/j.wasman.2016.08.009>.
- [19] O. Arpa, R. Yumrutas, A. Demirbas, Production of diesel-like fuel from waste engine oil by pyrolytic distillation, *Appl. Energy* 87 (2010) 122–127, <http://dx.doi.org/10.1016/j.apenergy.2009.05.042>.

- [20] G.J. Song, Y.C. Seo, D. Pudasainee, I.T. Kim, Characteristics of gas and residues produced from electric arc pyrolysis of waste lubricating oil, *Waste Manage.* 30 (2010) 1230–1237, <http://dx.doi.org/10.1016/j.wasman.2009.10.004>.
- [21] S.S. Lam, A.D. Russell, H.A. Chase, aPyrolysis using microwave heating: a sustainable process for recycling used car engine oil, *Ind. Eng. Chem. Res.* 49 (2010) 10845–10851, <http://dx.doi.org/10.1016/j.energy.2010.03.033>.
- [22] H. Guo, F. Peng, H. Zhang, L. Xiong, S. Li, C. Wang, B. Wang, X. Chen, Y. Chen, Production of hydrogen rich bio-oil derived syngas from co-gasification of bio-oil and waste engine oil as feedstock for lower alcohols synthesis in two-stage bed reactor, *Int. J. Hydrog. Energy* 39 (2014) 9200–9211, <http://dx.doi.org/10.1016/j.ijhydene.2014.04.008>.
- [23] N. Akiya, P.E. Savage, Roles of water for chemical reactions in high-temperature water, *Chem. Rev.* 102 (2002) 2725–2750, <http://dx.doi.org/10.1021/cr000668w>.
- [24] A. Kruse, E. Dinjus, Hot compressed water as reaction medium and reactant. 2. Degradation reactions, *J. Supercrit. Fluids* 41 (2007) 361–379, <http://dx.doi.org/10.1016/j.supflu.2006.12.006>.
- [25] A. Kruse, Review: supercritical water gasification, *Biofuels, Bioprod. Bioref.* 2 (2008) 415–437, <http://dx.doi.org/10.1002/bbb.93>.
- [26] A. Kruse, Hydrothermal biomass gasification, *J. Supercrit. Fluids* 47 (2009) 391–399, <http://dx.doi.org/10.1016/j.supflu.2008.10.009>.
- [27] P. Casademont, L. Cardozo-Filho, E. Meurer, J. Sánchez-Oneto, J.R. Portela, Gasification of olive oil mill waste by supercritical water in a continuous reactor, *J. Supercrit. Fluids* 142 (2018) 10–21, <http://dx.doi.org/10.1016/j.supflu.2018.06.001>.
- [28] J. Xu, J. Kou, L. Guo, H. Jin, Z. Peng, C. Ren, Experimental study on oil-containing wastewater gasification in supercritical water in a continuous system, *J. Hydrog. Energy* 44 (2019) 15871–15881, <http://dx.doi.org/10.1016/j.ijhydene.2018.10.069>.
- [29] A. Kupareva, P. Mäki-Arvela, H. Grénman, K. Eränen, R. Sjöholm, M. Reunanen, D.Y. Murzin, Chemical characterization of lube oils, *Energy Fuels* 27 (2012) 27–34, <http://dx.doi.org/10.1021/ef3016816>.
- [30] E. Förster, J. Becker, F. Dalitz, B. Görling, B. Luy, H. Nirschl, G. Guthausen, NMR investigations on the aging of motor oils, *Energy Fuels* 29 (2015) 7204–7212, <http://dx.doi.org/10.1021/acs.energyfuels.5b02164>.
- [31] E. Dominguez-Rosado, J. Pichtel, Chemical characterization of fresh, used and weathered motor oil vis GC/MS, NMR and FTIR techniques, *Proc. Indiana Acad. Sci.* 112 (2003) 109–116.
- [32] D. Mao, H. Van de Weghe, R. Lookman, G. Vanermen, N. De Brucker, L. Diels, Resolving the unresolved complex mixture in motor oils using high-performance liquid chromatography followed by comprehensive two-dimensional gas chromatography, *Fuel* 88 (2009) 312–318, <http://dx.doi.org/10.1016/j.fuel.2008.08.021>.
- [33] F.C.Y. Wang, L. Zhang, Chemical composition of group II lubricant oil studied by high-resolution gas chromatography and comprehensive two-dimensional gas chromatography, *Energy Fuels* 21 (2007) 3477–3483, <http://dx.doi.org/10.1021/ef700407c>.
- [34] A. Sanchez-Hernandez, N. Martin-Sanchez, M.J. Sanchez-Montero, C. Izquierdo, F. Salvador, Effect of pressure on the gasification of dodecane with steam and supercritical water and consequences on H₂ production, *J. Mater. Chem. A Mater. Energy Sustain.* 6 (2018) 1671–1681, <http://dx.doi.org/10.1039/C7TA09659C>.
- [35] A.B.A. Ibrahim, H. Akilli, Supercritical water gasification of wastewater sludge for hydrogen production, *Int. J. Hydrog. Energy* 44 (2019) 10328–10349, <http://dx.doi.org/10.1016/j.ijhydene.2019.02.184>.
- [36] M. Watanabe, H. Hirakoso, S. Sawamoto, T. Adschiri, K. Arai, Polyethylene conversion in supercritical water, *J. Supercrit. Fluids* 13 (1998) 247–252, [http://dx.doi.org/10.1016/S0896-8446\(98\)00058-8](http://dx.doi.org/10.1016/S0896-8446(98)00058-8).
- [37] G. Brunner, Reactions in hydrothermal and supercritical water, *Supercrit. Fluid Sci. Technol.* 5 (2014) 265–322, <http://dx.doi.org/10.1016/B978-0-444-59413-6.00005-4>.
- [38] M.J. Cocero, Supercritical water processes: future prospects, *J. Supercrit. Fluids* 134 (2018) 124–132, <http://dx.doi.org/10.1016/j.supflu.2017.11.018>.
- [39] A. Kruse, N. Dhamen, Water—a magic solvent for biomass conversion, *J. Supercrit. Fluids* 96 (2015) 36–45, <http://dx.doi.org/10.1016/j.supflu.2014.09.038>.
- [40] N. Martin-Sanchez, M.J. Sanchez-Montero, C. Izquierdo, F. Salvador, Conversion of a resistant pollutant, phenol, into green fuels by gasification using supercritical water compressed up to 1000 bar, *React. Chem. Eng.* 2 (2017) 799–810, <http://dx.doi.org/10.1039/C7RE00081B>.
- [41] N. Simsek-Kus, Organics reactions in subcritical and supercritical water, *Tetrahedron* 68 (2012) 949–958, <http://dx.doi.org/10.1016/j.tet.2011.10.070>.
- [42] C.M. Huelsman, P.E. Savage, Reaction pathways and kinetic modeling for phenol gasification in supercritical water, *J. Supercrit. Fluids* 81 (2013) 200–209, <http://dx.doi.org/10.1016/j.supflu.2013.05.012>.
- [43] T.L.K. Yong, Y. Matsumura, Kinetic analysis of guaiacol conversion in sub- and supercritical water, *Ind. Eng. Chem. Res.* 52 (2013) 9048–9059, <http://dx.doi.org/10.1021/ie4009748>.
- [44] D. Castello, A. Kruse, L. Fiori, Supercritical water gasification of hydrochar, *Chem. Eng. Res. Des.* 92 (2014) 1864–1875, <http://dx.doi.org/10.1016/j.cherd.2014.05.024>.