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# Supercritical fluid technology in biodiesel production: pilot plant design and operation

**Abstract:** The profitability of biodiesel is nowadays limited by the price of raw materials, which require high purity standards to be employed in conventional production processes. To overcome this problem, the transesterification of triglycerides in alcohol supercritical conditions could be conveniently used: the non-catalytic nature of this process allows the use of recycled raw materials, which are cheaper. To this end, a pilot scale plant for the continuous production of biodiesel in supercritical conditions was designed, manufactured and operated. In this research paper, rapeseed oil and bioethanol were used as raw materials, and the investigated temperatures were between 200 and 340°C, the pressure between 150 and 240 bar, and the alcohol-to-oil ratio ranged between 9 and 100. The best fatty acid ethyl ester (FAEE) yields were obtained at 340°C, 240 bar and a molar ratio of 42, which is line with easier-to-control lab-scale tests in batch conditions found in the literature. This encourages widening of the operating conditions to further improve the maximum achievable yields for the rapeseed oil-ethanol system.

**Keywords:** biodiesel; catalyst; non-catalytic; supercritical fluid; transesterification.

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## 1 Introduction

### 1.1 Biodiesel production routes

Biodiesel has several advantages over petroleum-derived diesel: it is biodegradable, non-toxic, sulfur-free, aromatic-free and can be produced from a number of renewable feedstocks, such as fresh [1–5] or waste [6, 7] vegetable oils and animal fats [8, 9]. Among oils, both edible (mostly from canola, soybean and palm [1–2]) and non-edible ones

(*Madhuca indica*, *Jatropha curcas*, *Jatropha gossypifolia* and *Pongamia pinnata* [3–5]) can be used to this end; although the latter are still not at a commercial stage, they are being more and more investigated, since they avoid the competition between food and fuel, and they are generally extracted from plants that can be cultivated in arid or marginal lands, which are unsuitable for conventional agriculture.

The blend of diesel with biodiesel, from 5% to its full substitution, to be used as fuel in compression ignition engines, has been carried out in several comparative studies [10–13], focused on both performance and emissions. In terms of engine power output, no difference is observed at biodiesel volumetric concentrations below 5%; in contrast, around 10% power reduction is recorded with pure biodiesel, especially at high engine loads, due to its slightly lower calorific value as compared to conventional diesel [10]. As far as the emissions are concerned, biodiesel produces substantially lower amounts of CO, HC and soot: -50%, -70% and -50% with pure biodiesel, respectively, which slightly decreases to -12%, -20% and -12% for a diesel with just a 20% biodiesel content [13]. These are average values, but more than 80% particulate matter emission reduction was recorded in tests with pure biodiesel [14]. These emission reductions are reached at the price of a modest 10% NO<sub>x</sub> emission increase for pure biodiesel, which becomes close to zero with a 20% biodiesel content [13].

The most common way to obtain biodiesel is the trans-esterification of triglycerides with an alcohol (generally methanol due to its high reactivity and low cost), which produces glycerin as a by-product, or the esterification of fatty acids with an alcohol, with the production of water. When a methyl group constitutes the terminal part of the chain, biodiesel is also known as fatty acid methyl ester (FAME). A less reactive alcohol is ethanol, which leads to fatty acid ethyl esters (FAEE); however, the interest towards this solution is high due to the possibility of producing a fully renewable fuel, i.e., from vegetable oils and bio-derived ethanol, thus not resorting to methanol which comes from fossil oil.

If the free fatty acids (FFA) content in the starting vegetable oil is lower than 1–3%, the production process involves directly the step of trans-esterification of the

triglyceride with an excess of alcohol, most commonly in a molar ratio two times higher the stoichiometric value if methanol is used, and using an alkali as the catalyst (i.e., KOH). The reaction is carried out at around 60°C and the yield is close to 100%. This represents the conventional, and worldwide employed, biodiesel production process [15, 16].

If vegetable oils naturally occurring with high FFA content, or waste oils (such as the ones subjected to thermal degradation, i.e., waste cooking oils), are employed, the presence of an alkali leads to the saponification of the FFA, and the consequent loss of valuable material. In addition, the water released during the esterification of FFA inhibits the trans-esterification of the triglyceride. Alternatively, an acid catalyst can be used, such as sulfuric acid if the reaction is carried out in homogeneous form [17], or supported heterogeneous catalyst (such as in the well-known Esterif<sup>HTM</sup> IFP process [18]) to avoid the subsequent separation of the catalyst. The acid-catalyzed trans-esterification has a lower reaction rate, therefore a two-stage process can be devised: an esterification of FFA in acid medium (often carried out at temperatures up to 200–250°C to speed up the process), followed by the trans-esterification of triglycerides in KOH medium. High yields can be obtained with the combination of these two steps [19].

Another concept for the valorization of the oils with high FFA concentration is the following: first, the triglycerides are hydrolyzed to FFA, and then the resulting FFA are esterified to FAME or FAEE. This scheme appears to be a faster route, and has the advantage of avoiding a sequence of acid and then basic catalysis, which requires two steps of neutralization. Reactive distillation with heterogeneous acid catalysts has been proposed to undertake the esterification step [20].

Finally, the most innovative solution is to carry out the reaction under alcohol supercritical conditions [21], which enhances the mutual miscibility of the oil and the alcohol, and fosters the reaction rate leading to biodiesel through both FFA esterification and triglyceride trans-esterification with the alcohol, all in one step [22, 23]: this avoids the use of a catalyst, thus bypassing the saponification reaction induced by the alkali in the presence of FFA, or the slow reaction rates peculiar to sulfuric acid-based systems. In this way, neither water nor FFA content affects the ester yield [24]. In fact, the production of biodiesel under supercritical conditions is seen as a breakthrough technology for a competitive exploitation of high FFA content oils, and especially waste oils, which are in this way revalorized. Methanol supercritical conditions have also been devised for the esterification of FFA, in the

above described sequence hydrolysis-esterification [25], in order to reduce the severity of the required supercritical conditions (270°C and 7 MPa) [26].

Even though the majority of research papers deal with supercritical trans-esterification with alcohols [6, 21, 22, 27], which does not avoid the production of glycerol, a trans-esterification process with supercritical methyl acetate has recently been proposed [28, 29], and developed within the Copiride project at the lab-scale [30]. This process leads to FAME and triacetine as products, the latter being much more valuable than glycerin on the market.

The possibility of exploiting variegated feedstock through innovative catalytic and non-catalytic supercritical processes, could pave the way for a wider exploitation of biodiesel.

## 1.2 Ethanol as the transesterification agent

The selection of the transesterification agent is based on the consideration of cost and performance. The application of FAEE is also more beneficial than that of FAME if being viewed from the environmental consideration: ethanol can be prepared from agricultural renewable feedstock, thereby gaining total independence from petroleum-based alcohols. Moreover, ethanol, as an extraction solvent, is preferable to methanol because of its much higher dissolving power for oils. For this cause, ethanol is sometimes used as a suitable alcohol for the transesterification of vegetable oils. The greatest number of vegetable oil ethanolysis research studies have been done in the South America countries, especially in Brazil, which is one of the greatest producers of ethanol from biomass in the world [31].

The fuel qualities of alkyl esters have received varying evaluations in terms of alcohol used. Some authors have stated that higher or branched alcohols can generate biodiesel with better fuel characteristics. Some studies reported that FAEE and FAME are similar in heat content, but FAEE is slightly less viscous than methyl ester. Therefore, producing ethyl esters rather than methyl esters is of great interest due to the entirely agricultural nature of the ethanol, and the extra carbon atom provided by the ethanol molecule slightly increases the heat content and the cetane number. Also, FAEE have cloud- and pour-points that are lower than the methyl esters, which improves the ignition start in cold conditions [31].

Different processes for FAEE production have been investigated in order to employ various kinds of catalyst such as acid [32–34], alkali [35, 36] and enzymes in the

transesterification with virgin vegetable oil, waste oil [37] or microalgae [37]. The alkali process gives a high purity and high yield of biodiesel in a short reaction time but is not suitable for oils with high FFA content. For such categories of oils, acid esterification followed by alkali transesterification can be used to decrease the high FFA content and to improve the biodiesel yield. However, the long reaction times and low catalyst recovery are an issue for this process. Enzyme catalytic transesterification requires longer reaction times. To overcome these disadvantages, non-catalytic transesterification under supercritical conditions is proposed as an alternative method to prepare FAEE.

Madras et al. [21] reported the highest conversion of sunflower oil with supercritical ethanol compared to methanol when performing experiments over the temperature range of 200–400°C at a constant pressure of 20 MPa, methanol to oil ratio 40:1, reaction time of 40 min. The reason for the higher yield of FAEE can be explained by the solubility of the oil in the system. In the supercritical state, there is only a single phase in the mixture of reactants. The solubility of ethanol is closer to that of oil than of methanol; thereof, the conversion is higher in the case of ethanol compared to methanol.

An optimization study on ethanol supercritical conditions was carried out by Gui and co-workers [38]. The reaction was performed in a batch-type tubular reactor with palm oil employed as feedstock for a specific duration ranging from 2 to 30 min and the temperature was screened by a PID controller. This study focused on the effects of the individual parameters during the reaction. It was reported that an optimal FAEE yield of 83.1 wt% was achieved at a temperature of 349°C, an ethanol to oil ratio of 33, and a reaction time of 29 min. The yields, obtained at the investigated reaction conditions in this work were lower than those of other researchers, which is very crucial in terms of the economic viability to commercialize this process.

In a new approach to reduce the intensity of the operating conditions, Santana et al. [39] employed a co-solvent (CO<sub>2</sub>) along with ethanol to prepare biodiesel under supercritical conditions in a fixed-bed reactor. The highest yield of biodiesel was recorded at a temperature of 200°C, reaction time of 4 min, a molar ratio of 1:25 and a pressure of 20 MPa. The addition of CO<sub>2</sub> is the main reason allowing the lower temperature, and can lead to the reduction of the operating costs.

A research team at Oregon State University (US) [40] made a break-through for continuous production of biodiesel with tin-based catalysts with supercritical ethanol and methanol. The catalyst was applied to 50–250 µm

stainless steel plasma powder, then tested with six different kinds of oil. With all type of oils, the conversion was >90% under the following operating parameters: temperature of 305°C, pressure of 17.3 MPa and ethanol to oil ratio of 30:1 and residence time of 8 min.

Within the framework of the Copiride project, a pilot-scale plant for triglyceride trans-esterification in supercritical conditions was designed and manufactured.

The plant was successfully operated for the production of biodiesel from rapeseed virgin oil, with bioethanol as the trans-esterification agent, without the use of any catalyst (although future investigations could comprise it), with the purpose of achieving a fully bioderived and renewable fuel, obtained at a pilot-scale in continuous regime and supercritical conditions.

## 2 Experimental

The synthesis of FAEE was carried out with the following raw materials: ethanol with a purity of 99.9% (64-17-5), purchased from Girelli Alcol srl, Milan, Italy, and rapeseed oil (8002-13-9), purchased from Gioma Varo srl, Brugherio (MB), Italy. All reagents were used without prior purification.

The experiments of biodiesel production in supercritical conditions were carried out with a continuous plant, whose main features are summarized in Table 1: its purpose is the continuous non-catalytic transesterification of vegetable oil with ethanol (although methanol could be used as well) under supercritical conditions (ethanol critical point: 241°C and 63 bar), under controlled temperature, pressure and oil/alcohol molar ratio.

The main unit operations carried out within the plant are schematized in the block diagram (BD) of Figure 1, while the full piping and instrumentation diagram (P&ID) is depicted in Figure 2.

The oil from the reservoir is heated to 40°C prior to being fed to the plant, due to its high viscosity at ambient temperature (37 cSt). The liquid alcohol is pressurized in P-102 (from Iwaki Italia srl, Milan, Italy), and then directed to the main pump P-101 (from Lewa srl, Rho (MI), Italy) for liquid mixture compression up to the nominal pressure,

**Table 1** Operating ranges of the plant.

Temperature range	250–400°C
Pressure range	150–250 bar
Inlet flow rate	15 l/h liquid feed (oil+alcohol)
Productivity	≈6 l/h FAME/FAEE
Alcohol/oil molar ratio	1–100

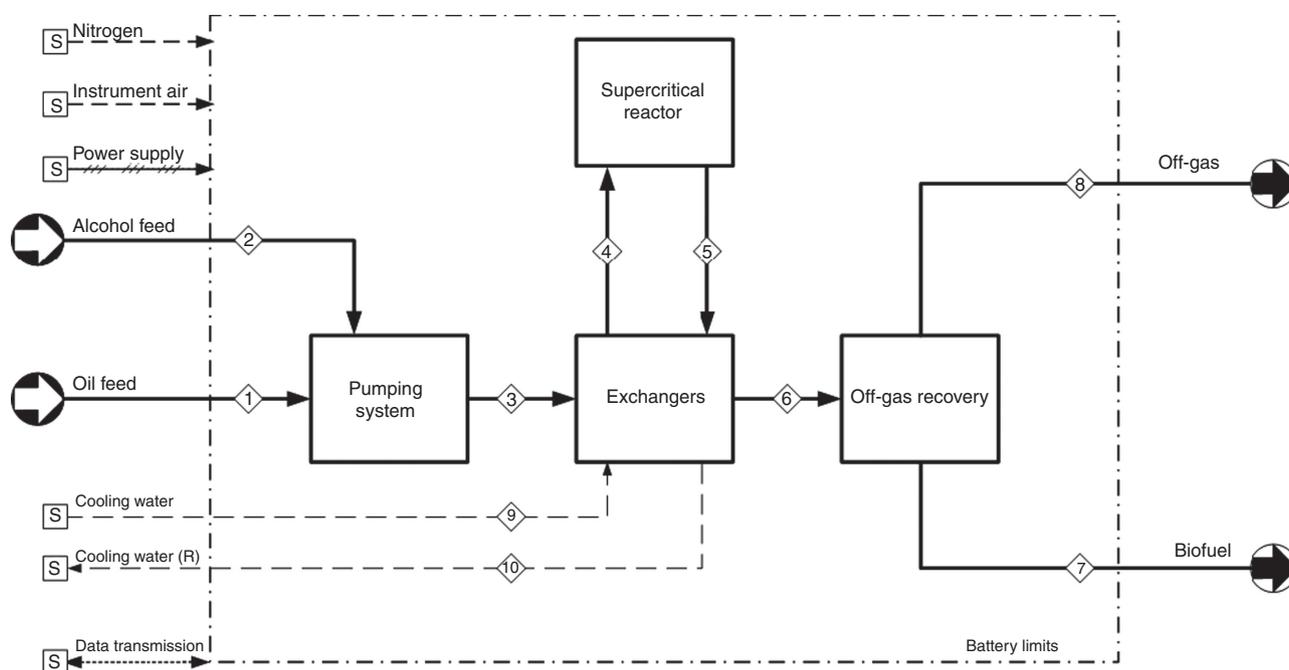


Figure 1 Block diagram of the plant.

where the oil and the alcohol are mixed. The individual flow rates of the oil and alcohol are regulated to the desired values by means of inverters in P-101 and P-102, in order to vary both the total flow rate of the liquid mixture, and the alcohol-to-oil molar ratio.

The compressed liquid alcohol-oil mixture enters a static mixer (M-101), and then is fed to the pre-heater (E-102a): this tube bundle of this heat exchanger comprises 12 tubes, with an internal diameter of 19 mm and a total length of 4170 mm, including the distributor system. The heating fluid, which is fed to the shell side, is a circulating diathermal oil (Downtherm A), whose temperature is regulated by the electrical heater E-104 (from Masterwatt srl, Pianezza (TO), Italy) up to a maximum of 400°C, and the circulation flow rate in the closed loop is ensured by a control unit PU-102 (by Tempco srl, Desio (MB), Italy).

The alcohol-oil mixture enters the reactor R-101 (from High Pressure Equipment Co., Erie, PA, USA), which is a dismantlable tube for rapid inspection, without the necessity of welding and re-certification after each maintenance, which is able to withstand pressures up to 330 bar. The internal diameter of the tubular reactor is 8.9 mm, while its length is 1520 mm. The axial temperature of the reactor is tuned through electric resistances E-101 (from Watlow Italy srl, Corsico (MI), Italy). The reactor is filled with SiC cubic pellets, of 10 mm diameter, to reduce the phases' segregation effects and preferential paths.

The mixture flowing out from the reactor is cooled in the heat exchanger E102-b, which is a twin of E-102a;

the cooling fluid is the diathermal oil itself, which comes from the circulating loop and is then fed to E-104. Further cooling of the process fluid down to around 60°C is carried out in E-103, whose cooling fluid is water at ambient conditions. The number and diameter of the tubes in E-103 are analogous to the ones of E-102a and E-102b, while their length is 1705 mm.

Lastly, the fluid enters the separation section, where pressure is reduced to ambient conditions through the expansion valve PY-101, after which either sampling of the fluid containing both reactants and products could be performed, or the fluid is conveyed to a decanter for two-phase separation (V-101).

The plant was operated at several conditions of temperature, pressure and alcohol-to-oil molar ratio. The full set of conditions is presented in Table 2.

As can be seen, the effect of the SiC pellets which fill the reactor was also investigated, in order to clarify whether they have a promoting effect in terms of fluid mixing, or they only affect the residence time in the reactor.

The total flow rate was equal to 0.25 l/min and was kept constant throughout all tests; the corresponding residence time in the reactor was 17 min in the presence of the filling, given the estimated 68% void fraction of the packed SiC pellets, while it was 25 min in the absence of it.

The product was sampled after the expansion valve and before the decanter, and both the polar and apolar phases were analyzed in terms of ethyl ester content: in particular the content of ethyl oleate, ethyl palmitate,

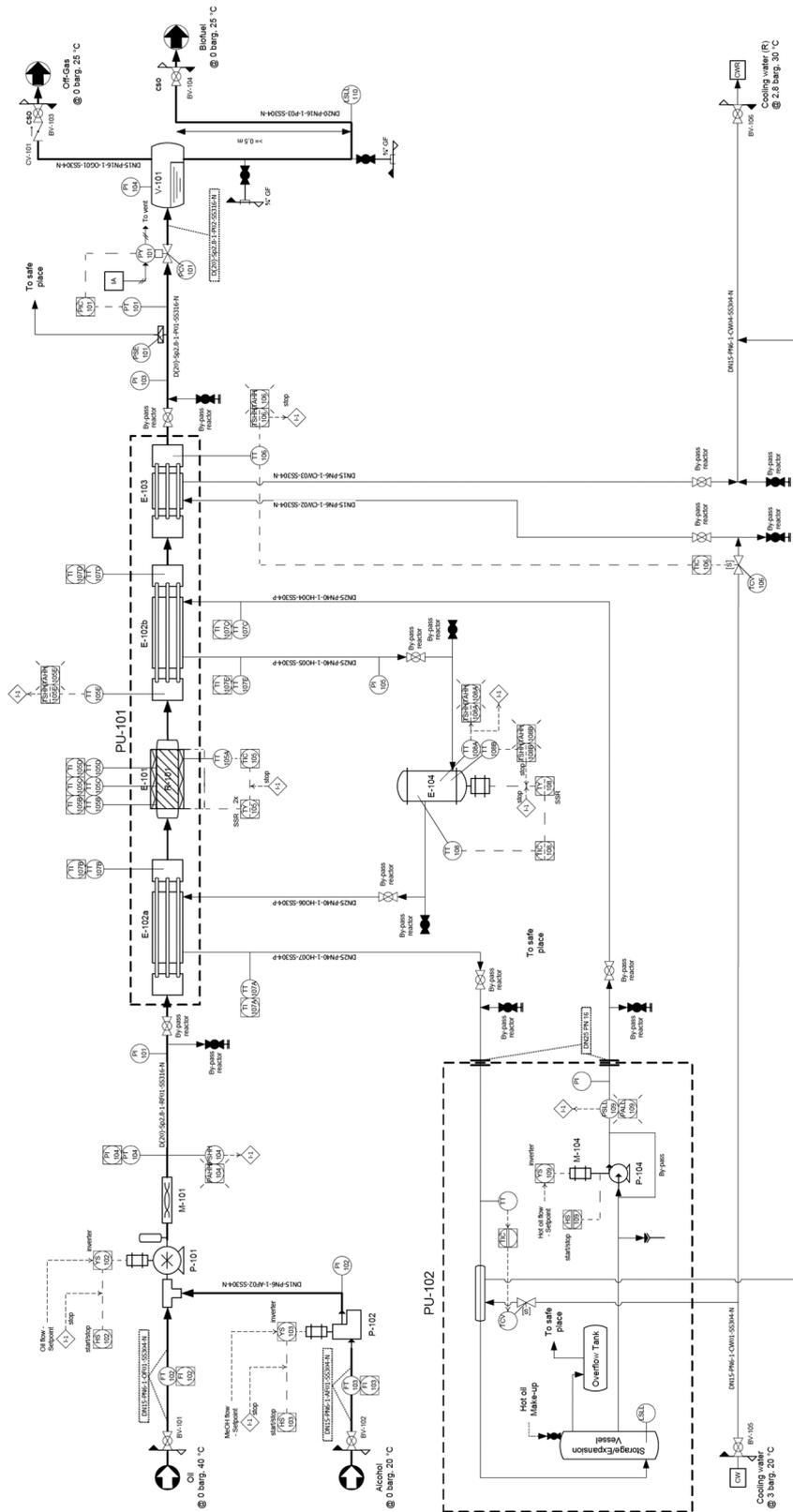


Figure 2 Piping and Instrumentation diagram of the plant.

**Table 2** Operating conditions of the tests.

Temperature (°C)	Pressure (bar)	Total flow (l/min)	Molar Ratio (alcohol/oil)	Parameter of interest
300	200	0.25	42	Reference conditions
200	200	0.25	42	Temperature
250	200	0.25	42	
340	200	0.25	42	
300	240	0.25	42	Pressure
300	170	0.25	42	
300	150	0.25	42	
300	200	0.25	9	Alcohol/oil molar ratio
300	200	0.25	22	
300	200	0.25	100	
300	200	0.25	42	Without reactor filling

ethyl stearate and ethyl linoleate was measured by HPLC, since the triglycerides of rapeseed oil mainly contain their corresponding fatty acids.

### 3 Results and discussion

The reference conditions of the tests were: pressure of 200 bar, temperature of 300°C at the reactor inlet, and an alcohol-oil molar ratio of 42. Based on the analysis of the fresh alcohol-ethanol mixture composition, and of the weight concentrations of FAEE at the outlet, the calculated FAEE yield was 11.9%.

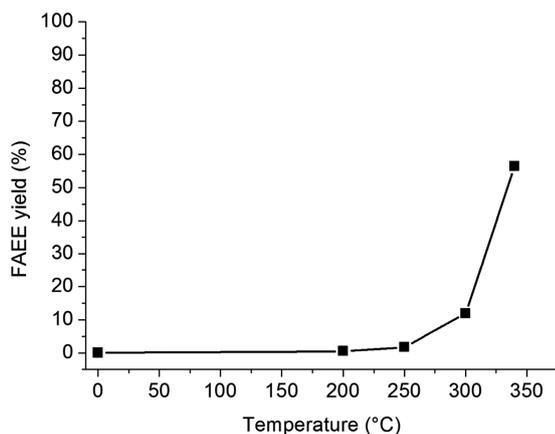
Figure 3 shows the effect of temperature between 200°C and 340°C on the FAEE yield: at sub-critical conditions ( $T=200^{\circ}\text{C}$ ) the yield was null, and still negligible slightly above the ethanol critical point ( $T=250^{\circ}\text{C}$ ), the latter being below 2%. Conversely, at 340°C, the FAEE yield was greatly increased to up to 56.4%. We observed that temperature has a very positive effect on FAEE yield,

especially at temperatures higher than 300°C, following a non-linear trend. This is consistent with the results reported by Saka and Kusdiana [22], although the tests were carried out with methanol, in which a maximum operating temperature of 380°C was used to avoid FAME degradation.

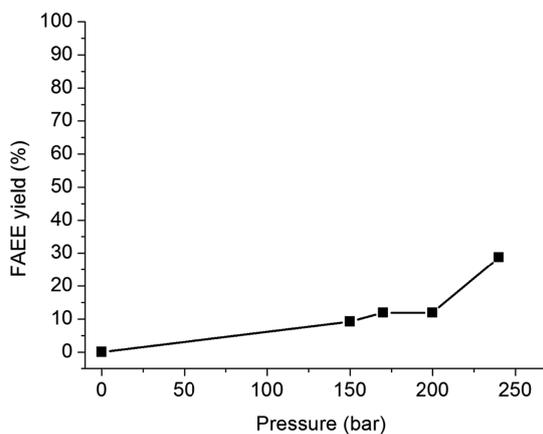
The effect of pressure is depicted in Figure 4, where the pressure is varied from 150 bar to 240 bar. A beneficial effect of increasing the pressure of the system was noticed, since the FAEE yield steadily increases: 9.2% at 150 bar, 11.7% at 170 bar, 11.9% at 200 bar and 28.7% at 240 bar.

The combined effect of the temperature and pressure at supercritical conditions is clear in increasing the miscibility of the polar (alcohol) and apolar (oil) phases, which affects the overall kinetics of the transesterification reaction.

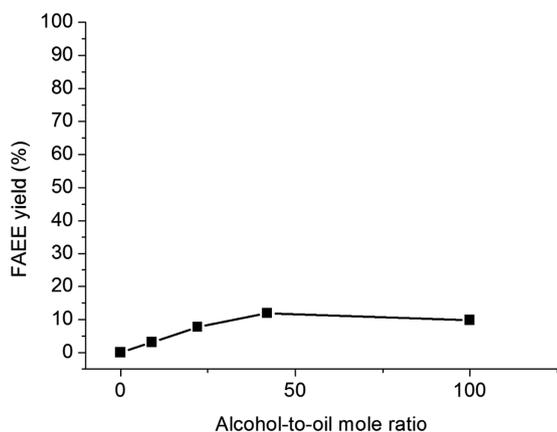
Finally, reactions were carried out at 300°C and 200 bar, at different alcohol-oil molar ratios ranging from 9 to 100, with a constant residence time of 17 min. From Figure 5 one can observe that an excess of alcohol is favorable to



**Figure 3** FAEE yield vs. temperature (pressure of 200 bar, alcohol-to-oil ratio of 42, with SiC reactor filling).



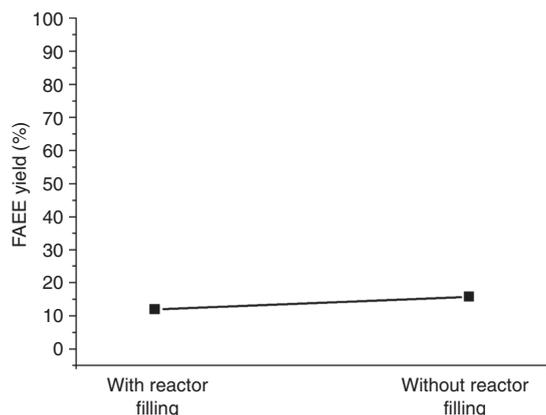
**Figure 4** FAEE yield vs. pressure (temperature of 300°C, alcohol-to-oil ratio of 42, with SiC reactor filling).



**Figure 5** FAEE yield vs. alcohol-to-oil molar ratio (temperature of 300°C, pressure of 200 bar, with SiC reactor filling).

FAEE yield: the conversion at a molar ratio equal to 9 was only 3.7%, while it increased to 7.6% at 22, up to 11.9 at 42. However, further increase of the ethanol concentration produced only a diluting effect, given the 9.8% FAEE yield obtained at a ratio equal to 100. This behavior could be explained by the fact that the reaction kinetics can be assumed to be of the first order with respect to the oil concentration at high alcohol/oil ratios, due to the insignificant changes in the alcohol concentration during the reaction. Although the increase of ethanol concentration shifts the equilibrium towards the products, the reaction kinetics could be depressed by such a low concentration of oil at a molar ratio of 100.

Figure 6 shows the effect of the reactor filling on the FAEE yield, which was evaluated in the presence and absence of SiC pellets. The obtained results showed that the FAEE yield increased in the absence of SiC pellets, and



**Figure 6** FAEE yield in the presence or absence of the SiC reactor filling (temperature of 300°C, pressure of 200 bar, vs. alcohol-to-oil molar ratio of 42).

reached 15.7%, slightly higher than the standard condition with the filled reactor, which was equal to 11.9%. This evidence suggests that the higher residence time of the reacting mixture, due to the absence of the filling, has a beneficial effect on the total conversion; conversely, the mixing promotion given by the pellets is of minor effect, especially when supercritical conditions are fully reached and the mutual miscibility of the reacting phases is satisfactory.

The presented results show that the best achieved oil conversions were reached at temperature conditions of 340°C and pressures of 240 bar; the employed alcohol-to-oil ratio was beneficial up to 42, while greater values were of negligible effect. Finally, the effect of the residence times was extremely important, since the reactor filling avoidance (which corresponded to roughly a 30% residence time increase) determined a relevant improvement in the FAEE yield. This suggests widening the operating range of residence times by regulating the inlet flow rate of the oil and ethanol.

It is worth analyzing the conversion efficiency of this process to produce biodiesel from rapeseed oil and ethanol, at the operating conditions for the best conversion case. At 340°C, 200 bar, and an alcohol-oil molar ratio of 42, the conversion was 56.4%: based on the 0.25 l/min feed to the plant (with individual flow rates of rapeseed oil and alcohol of 0.085 l/min and 0.165 l/min, respectively), this means a production of 3.32 l/h of FAEE. Considering an average lower heating value of 40.4 MJ/kg (value calculated based on ethyl oleate, which is the most abundant FAEE), and a density of 0.87 kg/l at ambient conditions, this translates into a chemical power of around 116.7 MJ/h, i.e., 32.4 kW<sub>th</sub>. Since the exothermic heat of reaction is very modest (around 80.9 kJ/kg<sub>ethyl-oleate</sub>, as a reference for FAEE, corresponding to <0.07 kW<sub>th</sub> at these conditions), all heat to perform transesterification should be provided, apart from heat integration, by external sources: in the case of the plant under investigation, the above mentioned electrical resistances around the reactor (E-101) and the electrical heater for diathermal oil heating (E-104) should be considered. The contribution of the electrical resistances is very modest, being 0.5 kW<sub>th</sub>, while E-104 accounts for 6 kW<sub>th</sub> at such conditions of temperature (340°C inside the reactor). This means that 6.5 kW<sub>th</sub> are consumed due to all heat requirements of the plant, including dispersion. In addition, compression of the feed impacts on the power needed by the plant by around 1.3 kW<sub>el</sub>. It can be derived that a thermal and an electrical power equivalent to around 20% and 4% of the total chemical energy stored in the produced biodiesel, respectively, are required by the current plant to perform the transesterification of oil and ethanol to FAEE.

One has to underline that the obtained results are in line with experiments in which ethanol was used as the transesterification agent [38, 41]: from batch experiments with ethanol and palm oil, it can be derived that a FAEE yield around 45% was obtained at a temperature of 350°C, molar ratio of 42 and reaction time of 17 min (the pressure being between 150 and 250 bar in those experiments). This is very encouraging because the pilot scale of this plant proved to be effective in replicating results obtained at a lower scale, which is extremely difficult given the greater issues of oil and alcohol homogenization, and, more importantly, in continuous mode.

From the same set of experiments, as stated in the introduction, it was found that significantly higher FAEE yields could be obtained only for higher residence times, i.e., 29 min allowed an oil conversion slightly above 80% at the same temperature and molar ratio conditions [38]. This will be the object of future experimentation.

Further investigations will also involve the use of hydrated ethanol (96% ethanol), due to the beneficial effect of water in small concentrations to hydrolyze triglycerides to fatty acids, which are then esterified to FAEE, which could increase the yield at low residence times (above 80% FAEE yield from rapeseed oil at 340°C, 250 bar, alcohol-to-oil molar ratio of 7 and residence time of 10 min [42]).

## 4 Conclusions

The search for sustainable synthesis pathways for biodiesel generation is still ongoing, although extensive research and development work on this topic has already led to a broad variety of process alternatives, utilizing different oil feedstock, alcohols, catalysts and process parameters.

This work presents the characteristics of a pilot-scale plant for the production of biodiesel, suited for supercritical condition synthesis. Supercritical transesterification

can easily treat feedstock that contains impurities or high FFA contents, which are both detrimental in catalytic processes. Conversely, the absence of any catalyst due to fostered reaction kinetics in supercritical conditions widens the window of potentially valuable triglyceride sources.

The plant was designed and manufactured within the framework of the Copiride EU project, with a high flexibility towards the feed and the desired operating conditions, and a nominal biodiesel productivity of 0.1 l/min.

Bio-derived ethanol was used as the transesterification agent, with the purpose of achieving a fully renewable biodiesel fuel. Starting from a reference condition of 300°C, 200 bar, alcohol-to-oil ratio of 42, which led to a FAEE yield of 11.9%, these parameters were varied to investigate their individual effect. The most relevant effect was given by the change in temperature, for which the FAEE yield reached 56.4% at 340°C, the other conditions being the same. The pressure increase was also beneficial towards the oil conversion, since at 240 bar (at 300°C and molar ratio of 42) the FAEE yield was 28.7%. As far as the molar ratio was concerned, it was found that its further increase above 42 did not lead to any improvement in the oil conversion. Finally, the residence time in the reactor was also evaluated, by operating the reactor without the internal pellet filling: the FAEE yield increased from 11.9% to 15.7%, but more “controlled” evaluations should be performed by manipulating the residence time through the total flow rate, which is planned as a future investigation.

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