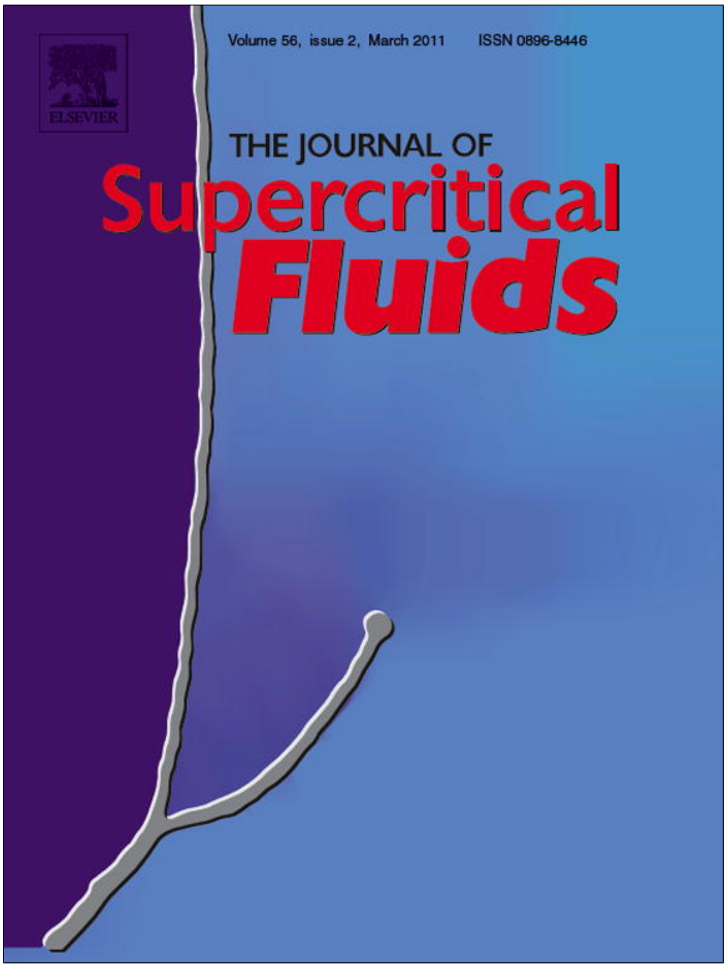

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Transesterification of rapeseed oil over acid resins promoted by supercritical carbon dioxide

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ABSTRACT

The methanolysis of rapeseed oil catalyzed by commercial styrene-divinylbenzene macroporous acid resins was performed in a batch reactor at 100–140 °C and 10–46 MPa to study the effect of supercritical carbon dioxide (scCO$_2$) on the performances of the process. Reaction temperatures of 120–140 °C were necessary to obtain high enough yields of fatty acid methyl esters. Upon addition of scCO$_2$ faster transesterification kinetics was obtained also at the lowest investigated operating pressure (10–11 MPa), working in two fluid phase systems. Experiments performed changing the reaction time indicated that most of the esters were formed during the first 3 h. When the pressure was increased at 38–46 MPa, the fluid phases merged in a single one without significant modification of the performances of the process.

The enhancement effect of scCO$_2$ on the transesterification kinetics is tentatively discussed in terms of modification of the phase behaviour of the reaction system and swelling of the polymeric acid resin.

1. Introduction

Transesterification of triglycerides (TGs) with low molecular weight alcohols can be used to prepare a liquid stream suitable as non petroleum based feed for diesel engine. The process is already applied at the industrial scale using vegetable oils as feedstock, methanol as alcohol and a base such as sodium hydroxide or methoxide as homogeneous catalyst [1,2].

To be effective this synthetic route requires the use of raw materials with low content of free fatty acids (FFAs) that are more expensive and adversely impact the total biodiesel cost [3]. Moreover the catalyst poses corrosion constraints for construction materials and its neutralization and separation from the product requires energy intensive unit operations that lead to the production of significant amount of aqueous waste. The use of homogeneous acid catalysts can prevent the soap formation that limits the maximum tolerable concentration of FFAs in direct base-catalyzed processes but does not solve the problems of the catalyst recovery and corrosion [4].

On these bases, the development of processes activated with heterogeneous acid catalysts could offer several advantages since catalyst segregation from the reaction mixture simplifies product separation and purification, decreases waste generation and avoids corrosion problems.

Solid acid catalysts have been investigated much less than their basic counterparts probably because it is generally assumed that their activity is too low to make them interesting for industrial exploitation [4–7].

In the literature studies on the utilization of zeolites, heteropolyacids and functionalized zirconia and silica are reported [7–12]. In the case of the zeolites, internal diffusion resistances are considered to limit significantly the rate of reaction. Zirconia and silica catalytic systems, giving interesting results, need to be activated at *T* higher than 170–200 °C. Heteropolyacids are active under mild conditions but are not yet fully characterized for what concern their long term stability and performances [8,13].

Sulfonated polymer matrixes are another class of heterogeneous catalysts that has been tested for the preparation of biodiesel. Among them styrene-divinybenzene copolymer sulfonated acid resins are particularly interesting because specific surface area, swelling capability and density of acid sites can be easily changed as a function of the copolymerization recipe and of sulfonation conditions. Additionally they are relatively inexpensive and are already applied in several industrial routes as catalysts or as ion exchangers for purifications [14,15].

These matrixes have been studied both for the esterification of FFAs [16–21] and for the transesterification of vegetable oils [22–24]. When methanolysis of TGs was carried out at temperature close to the boiling point of the alcohol, methanol to oil molar ratios higher than 100 were necessary to have high yields in methyl esters with relatively low reaction times.

In homogenous catalyzed transesterification processes, at the beginning of the reaction, the alcohol soluble catalyst and the oil

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Table 1
Main characteristics of strong acid resins used in this study.

Catalyst	Matrix	T_{max} (°C)	DWC (meq/g)	A_s (m^2/g)	D_p (Å)	V_p (mL/g)	ρ_s
Purolite CT275DR	Styrene-co-divinylbenzene 650–900 μm	145	5.2	20–40	400–700	0.4–0.6	1.2
Purolite CT169DR	Styrene-co-divinylbenzene 650–900 μm	145	4.7	35–50	250–425	0.3–0.5	1.2
Nafion SAC-13	Nafion perfluorinated polymer supported on silica	200	0.13	200–240	>100	>0.6	2.2

T_{max}, maximum working temperature; DWC, dry wet capacity; A_s, specific surface area; D_p, average pore diameter; V_p, pore volume; ρ_s, specific density.

Table 2
Fatty acid composition of the vegetable oil used in this study.

Fatty acid (C-length: no. = bonds)	16:0	18:0	18:1	18:2	18:3	20:1	22:1
% (w/w)	4.2	1.8	63.0	20.0	8.6	1.9	0.5

are segregated in different phases and mass transfer kinetics of the TGs can significantly affect the reaction rate. To overcome this drawback, it was proposed the utilization of a cosolvent agent that allowed to perform the reaction in a one-phase reaction system with significant intensification of the process [25]. Obviously, also an heterogeneously catalyzed reaction would enjoy some benefits by utilization of aforementioned synthetic strategy.

Supercritical carbon dioxide ($scCO_2$) has been proposed as reaction medium, in substitution of conventional organic solvents, to perform a wide range of heterogeneously catalyzed chemical reactions [26]. Such interest relies on the attractive chemical–physical and technical–economical properties that are typical of $scCO_2$. In fact, as all supercritical fluids, it exhibits a solvent strength that can be tuned with the density, quite high rates of mass and heat transfer, the elimination of gas–liquid mass transfer limitations. Such peculiarities can be transferred to liquid phases provided that a large amount of the gaseous component can be dissolved in the condensed system under pressurized conditions. By this approach it could be possible to operate in a multiphase reaction system at pressure values significantly lower than those necessary to achieve homogeneous conditions, solving problems related to the limited solubility of most substrates in $scCO_2$ [27].

Quite interestingly, dense CO_2 exhibits specific interactions with methanol significantly decreasing its polarity [28,29] and, in principle, playing a compatibilizing effect between the hydroxyl compound and the vegetable oil. Moreover, differently from liquid cosolvents, it can be easily removed at the end of the process by pressure release thus leaving unchanged the procedures for fuel purification.

Aim of this work is to study the effect of supercritical carbon dioxide, used as a solvent or as an expansion agent of the liquid system methanol/oil, on the transesterification of TGs catalyzed by commercial styrene-divinylbenzene sulfonic acid resins.

2. Experimental

2.1. Materials

Methanol (Aldrich HPLC grade) and carbon dioxide (99.998% purity Rivoira) were used without further treatment. Heptane (Chromasolv) from Aldrich and methyl heptadecanoate (puriss. p. a. ≥99.5%) from Fluka, were used, respectively, as diluent and internal standard for the GC analysis of the transesterified oil. Macroporous strong acid resin catalysts were kindly donated from Purolite (moisture content lower than 3%, w/w). Their code and main characteristics are summarized in Table 1 together with the properties of SAC-13 Nafion acid catalyst, purchased from Aldrich, and used for comparison. Refined rapeseed oil was obtained from Oleificio Zucchi S.p.A with a typical fatty acid composition that is reported in Table 2.

2.2. Reaction system and procedures

All transesterification experiments were carried out batchwisely in a three ports high pressure AISI 316 view cell (nominal volume of 50 mL), from Thar SCF. The autoclave was equipped with two 1.25 in. diameter sapphire windows with 180° orientation and the reaction mixture was stirred by a Teflon coated magnetic bar. The reactor was fitted with a pressure transducer (Barksdale UPA 3, estimated accuracy by calibration with a high-precision manometer of ±0.05 MPa) and a Pt100 thermal sensor, with an accuracy of ±0.3 °C, both mounted on the same port. One other port of the vessel was fitted with a Swagelock male connector closed by a cap to allow the loading of condensed components. The last opening was fitted with a high pressure needle valve to convey CO_2. The reactor temperature was kept constant by a heating mantle controlled by a PID electronic controller (Eurotherm). Total free volume of the assembled reactor was determined to be 54 ± 0.2 mL by several measurements with $scCO_2$ and argon at different masses, pressures, and temperatures using Span and Wagner equation of states for the pure components [30,31].

The use of the view cell allowed the operator to observe the phase behaviour inside the reactor during the whole duration of the reaction.

For a typical transesterification experiment, a weighed amount of the catalyst (10%, w/w with respect to the oil) was loaded through the opening of a window immediately before its closure. Then the selected amounts of rapeseed oil and methanol were delivered through the Swagelock connector. The masses of all these components were weighed by an electronic scale Sartorius LP 8200S, precision 0.01 g. Then the reactor was sealed and washed several times with low pressure gaseous CO_2. Liquid CO_2 was loaded at room temperature by means of an ISCO 250D syringe pump. Its amount was measured putting the cell on the aforementioned scale during the pressurization. Nominal density of the mixture was estimated at the end of the loading procedure as the ratio between the total masses of loaded fluid components (oil, methanol and CO_2) and the free volume of the vessel. The reactor was then connected to the heating mantle and heated up to the reaction temperature while the stirring was commenced. Blank experiments showed that catalyst activity is negligible below 100 °C. When the system reached that temperature the average heating rate was estimated to be 4 °C/min so that about 10 min were necessary to reach the highest temperature adopted in this study (140 °C). This short period was neglected in the computation of the reaction time that was considered to start when the system reached the selected reaction temperature. Reaction time was varied from 1 to 8 h.

2.3. Analytical techniques

At the end of each transesterification experiment, the reactor was cooled down to room temperature by removing the heating mantle and immersing the vessel in an ice/water bath (cooling time lower than 5 min). The view cell was carefully dried from any residual water and was slowly depressurized. Then the reactor was opened, the catalyst was separated by vacuum filtration and the residual biphasic system was recovered and evaporated at low pressure to remove unreacted methanol. The residual oil phase was extracted three times using a NaCl saturated aqueous solution (about 15 mL for each wash) and dried with anhydrous $MgSO_4$. This mixture was analyzed using an Agilent 7890 Gas Chromatograph (GC) equipped with a SUPELCO SP-2560 capillary column (fused silica, length 100 m, internal diameter 0.25 mm) using a Flame Ionization Detector (FID) and nitrogen with a purity of 99.999% as carrier gas. Calibration was done for fatty acid methyl esters (FAMEs) using methyl heptadecanoate as internal standard preparing solutions of known concentration by suitable dilution of a FAME standard mixture, C14–C22 18917-1AMP from Supelco.

Cumulative yield in methyl esters was computed according to Eq. (1)

$$Y = \frac{N_{\text{FAME}}}{3(W^0_{\text{oil}}/\text{PM}_{\text{oil}})} \tag{1}$$

where N_{FAME} is the total number of moles of free fatty acid methyl esters determined from the GC calibration, $W^0{}_{\text{oil}}$ is the initial mass of rapeseed oil loaded in the reactor and PM_{oil} its average molecular weight computed from composition reported in Table 2.

3. Results and discussion

3.1. Investigation of the phase behaviour of the reaction system

A detailed investigation of the phase behaviour of the ternary system rapeseed oil/methanol/carbon dioxide was behind the aim of this investigation. Anyway some spot experiments, useful for the analysis of the results of transesterification experiments, were performed. The solubility of rapeseed oil in $scCO_2$ is quite low and at 80 and 100 °C it was found lower than 0.12% (w/w) at pressures lower than 23 MPa [32].

The behaviour of the oil/CO_2 system was investigated in the same view cell used for methanolysis reactions. A weighed amount of tryglicerides (1.8 g) was loaded in a cylindrical glass vial. The cell was purged with low pressure CO_2 and liquid carbon dioxide was fed in such amount to reach 0.45 g/mL nominal density of the system. Then the vessel was heated to 80 °C recording the value of pressure every 5 min. After attainment of equilibrium condition, defined by stabilization of the cell pressure, the system was visually inspected. Pictures were taken to estimate the change in the height of the oil phase. Then the vessel was cooled to room temperature and further CO_2 was added before repeating all aforementioned steps.

The procedure was performed three times. In all cases the pressure inside the cell reached a stable value within 15 min from the attainment of the working temperature changing less than 1 MPa during this period. The volume of the liquid phase increased in the presence of CO_2 as summarized in Table 3. We wish to underline that, given the approximation of the adopted methodology, the estimated volumes must be taken only as an indication of the behaviour of the liquid phase. A clear expansion, close to 10% of the initial volume, was observed at 17.6 MPa. When the pressure was further increased at 21.4 MPa the expansion became 36% demonstrating that significant amount of CO_2 can be dissolved in the oil under adopted conditions. A further addition of carbon dioxide did not significantly alter the volume of the oil phase.

Table 3
Estimation of the effect of CO_2 on the expansion of rapeseed oil at 80 °C.

CO_2 (g)	P (MPa)	$V - V^0/V^0$ (%)
20.0	17.6	11
29.4	21.4	36
31.7	24.0	30

V is the volume of CO_2 expanded oil phase, V^0 is the initial volume of the oil phase.

Table 4
Recipes of systems studied in non reactive conditions.

System	Oil (g)	MeOH (g)	CO_2 (g)	CT275DR (g)
1	10	10.02	27.6	0
2	20.06	0	25.8	2.02

Other two experiments in non reactive conditions were carried out loading in the view cell oil, carbon dioxide and methanol or the catalyst, as reported in recipes in Table 4, and heating the system at 80 °C taking values of the pressure every 5 min.

In the case of the system 1, the pressure reached a stable value of about 33 MPa a few minutes after the temperature gained its final value and during this period the pressure decreased of about 0.5 MPa. Differently, in the case of system 2, about 1 h was necessary to obtain a stable pressure and its value decreased of about 3 MPa during this period. These results can be considered an indirect evidence that CO_2 dissolves not only in the liquid reactants but also in the catalyst phase reasonably giving a contribution to its swelling.

To obtain additional evidence of the swelling of the catalyst an experiment similar to that performed to study the expansion of the rapeseed oil was carried out. A cylindrical glass vial was loaded with 1.7 g of catalyst and inserted in the view cell. In the windowed reactor, outside the glass cylinder, were also loaded 20 g of rapeseed oil. The system was purged with CO_2 and heated at 80 °C. The equilibrium pressure reached a value of 1 MPa. After equilibration a picture of the catalyst bed was taken (Fig. 1a), then CO_2 was pumped to pressurize the system. After the loading, time was waited for system equilibration and pressure reached a final value of 15.8 MPa. Then a new picture was recorded (Fig. 1b) that confirmed the simultaneous expansion of both the oil and the catalyst bed.

3.2. Transesterification reactions in one fluid phase regime

The solvent power of supercritical fluids can be tuned changing the density of the mixture. To study the performances of the process in the absence of interfacial mass transfer resistances we performed a set of transesterification experiments at total nominal density of the system equal or higher than 0.74 g/mL and 100, 120 and 140 °C, loading an initial mass of oil of 8.62–8.69 g with a methanol to oil molar ratio higher than 27. Under these conditions, at all investigated reaction temperatures, the system was constituted by a single fluid phase where the solid catalyst was dispersed.

Collected results are summarized in Table 5 together with the outcomes of blank experiments performed without CO_2.

In the absence of CO_2, oil conversions after 8 h of reaction time increased significantly when the temperature was changed from 100 to 120 °C while it maintained substantially unchanged when the transesterification was carried out at 140 °C. The addition of carbon dioxide allowed us to enhance significantly the methyl ester yield that passed from 2.5 to 16.5% at 100 °C and from 24.6 to 55%

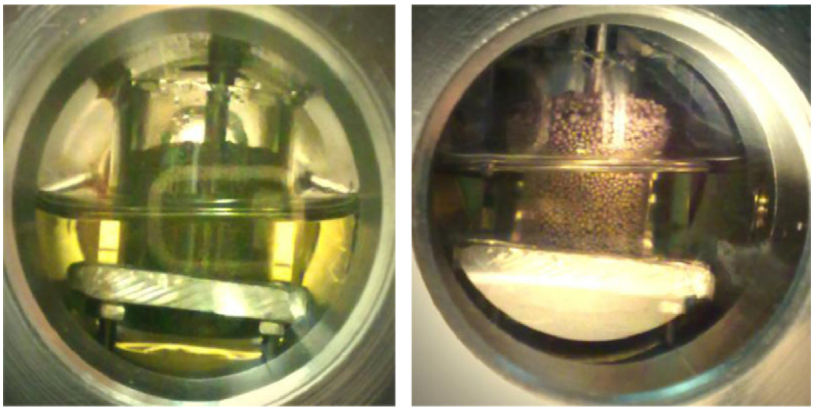

Fig. 1. Swelling of polymeric CT275DR catalyst pressurized with $scCO_2$ at 80 °C. (a) $P = 1.0$ MPa, (b) $P = 15.8$ MPa.

at the highest adopted reaction temperature. Moreover the yield always increased when the operative temperature was increased even if the effect tended to level off.

At 100 and 120 °C selected experiments were performed doubling the methanol to oil molar ratio and in both cases a reduction in the free fatty ester yield was observed.

In the case of solid acid catalyzed transesterification of esters and esterification of acids it was frequently found that an Eley–Rideal heterogeneous kinetic model, assuming as rate determining step the reaction between an adsorbed trygliceride and an alcohol molecule dissolved in the pore channel, matches quite well the experimental data [16,33–36]. The two molecules compete for protonation and chemisorption on the polar sulfonic groups of the resin, the hydroxyl compound being characterized by a more favourable equilibrium partitioning. Then the decrease in the kinetics of the reaction, that we observed when higher alcohol to oil ratios were used, could be attributed to a lower surface concentration of esters of glycerol and fatty acids when the methanol concentration in the fluid phase was increased.

As implicitly observed at the beginning of this section, the most intuitive explanation for the faster kinetics of the transesterification would be the modification of the phase behaviour of the system that was made homogeneous by the compatibilizing effect of dense carbon dioxide. Anyway the high pressures that were necessary to reach single phase condition adversely impact on the economics of the process in the perspective of its practical utilization.

Prompted by this consideration we decided to study the transesterification lowering the CO_2 loading in the reactor thus performing the process in biphasic fluid systems. This choice was also motivated by the scientific curiosity of better addressing the role of CO_2 in these systems.

3.3. Transesterification reactions in two fluid phase systems

A set of experiments was performed decreasing the amount of CO_2 loaded in the reactor. By this choice, at the investigated reaction temperatures of 120 and 140 °C, we obtained lower working pressures (Table 6). The phase behaviour of the system was visually inspected during the reaction. At room temperature the solid catalyst was in the presence of three fluid phases. It seems reasonable to presume that the heaviest, yellow coloured, was mainly constituted by the rapeseed oil, the lightest, transparent, was rich in carbon dioxide and the intermediate one, transparent too, rich in methanol.

During heating of the reactor the two heavier phases were intimately mixed by the stirring with consequent formation of an emulsion while the lightest was substantially segregated in the upper part of the vessel. When the MeOH/oil ratio was close to

Table 5
Acid resin catalyzed transesterification of rapeseed oil assisted by $scCO_2$ in one fluid phase systems.

Exp.	T (°C)	P^0 (MPa)	Oil (g)	MeOH/oil (mol/mol)	ρ (g/mL)	Y (%)
1	100	0.3[a]	10.1	27.4	0.37	2.5
2	100	37.9	8.63	27.7	0.83	16.5
3	100	43.9	8.63	55.3	0.85	6.1
4	120	0.6[a]	9.98	27.7	0.37	27.9
5	120	44.3	8.68	27.5	0.82	45.3
6	120	42.6	8.62	55.4	0.80	33.4
7	140	1.1[a]	10.00	27.7	0.37	24.6
8	140	45.8	8.69	27.7	0.74	55.0

T, reaction temperature; P^0, initial pressure; ρ, nominal density; Y, yield in methyl esters. Reaction time 8 h. Catalyst loading 10% w/w with respect to the oil.

[a] Experiments performed in the absence of CO_2.

Table 6
Acid resin catalyzed transesterification of rapeseed oil assisted by $scCO_2$ in two phase fluid systems.

Exp.	T (°C)	P^0 (MPa)	Oil (g)	MeOH/oil (mol/mol)	ρ (g/mL)	Y (%)
1	120	0.6[a]	9.98	27.7	0.37	27.9
2	120	19.6	8.65	27.7	0.57	50.4
3	120	9.7	8.64	27.7	0.44	45.6
4	140	1.1[a]	10.00	27.7	0.37	24.6
5	140	11.0	8.66	27.7	0.44	62.4

T, reaction temperature; P^0, initial pressure; ρ, nominal density; Y, yield into methyl esters. Reaction time 8 h. Catalyst loading 10% w/w with respect to the oil.

[a] Experiments performed in the absence of CO_2.

28, at investigated reaction temperatures, the catalyst was initially contacted with the emulsion that after a time that changed with the adopted conditions became homogeneous leading to the formation of a two fluid phase system.

When we studied the effect of the operating pressure at 120 °C, we found that yields in free fatty acid methyl esters were similar going form a one fluid phase (Exp. 5, Table 5) to a biphasic fluid reaction system both at 19.6 and at 9.7 MPa (Exp. 2 and 3, Table 6). The CO_2 loading greatly affected the time necessary to clarify the emulsion that increased from 50 to 210 min when the pressure decreased from 19.6 to 9.7 MPa. Also at the lowest investigated pressure a faster rate of formation of FAME was observed in comparison with that obtained in CO_2 free reactions (Exp. 1 and 3, Table 6).

The experiment performed with 0.44 g/mL nominal density was repeated at 140 °C. At this higher operating temperature, the pressure slightly increased reaching a value of 11 MPa and the two heavier phases merged in a single one after only 35 min. Similarly to what observed in reaction systems characterized by the presence of a single fluid phase in contact with the catalyst, when the temperature was increased from 120 to 140 °C in the two fluid phase system, an higher formation of esters was obtained since yields passed from 46 to 62%.

This result clearly indicates that acid resin catalysed transesterification of vegetable oil can be accelerated by the addition of limited amount of carbon dioxide to the system without the need of reaching the high pressure values necessary to operate in one fluid phase regime.

We wish to highlight that ester yields similar or even higher than those measured in this study were obtained at reaction temperature close to the normal boiling point of methanol using poly(styrene-co-divinylbenzene) sulfonated matrixes similar to Purolite CT275 [16,22,24,37].

Anyway in those studies operative conditions that significantly enhance the kinetics of the process were adopted i.e. much higher methanol to oil molar ratios and catalyst loadings or short alkyl chain triglycerides that are known to be much more active species in transesterification reactions catalyzed by sulfonic resins [38].

Available experimental data do not allow to give a clear explanation of the positive effect of low pressure CO_2 on the performances of the process. Anyway in the following we propose some reasons that could justify the observed result.

The catalyst adopted in this study is a sulfonated styrene-divinylbenzene copolymer with macropores. During its functionalization two populations of $-SO_3H$ groups are generated: one located on the exposed surface of the catalyst, the other constituted by sulfonic groups attached to aromatic rings buried in the bulk of the resin (Fig. 2).

The former can be reached by reactants overcoming external and internal mass transfer resistances only. The latter can be accessed only if the diffusion coefficient of methanol and triglycerides in the polymer matrix is high enough.

To support this consideration we can underline that when the transesterification was studied in membrane reactors equipped with bulk polymeric membranes an induction period correlated with the swelling kinetics of the matrix was observed [23].

Polar molecules such as methanol and glycerol are known to swell the acid resin and the extent of the volume expansion depends on the nature and concentration of the ionic groups, the density of crosslinks and the size and shape of solvation shell [16]. In this case, the volume expansion of the resin is generally attributed to an increase in the local concentration of polar molecules inside pores. The driving force for this phenomenon is considered the difference in the osmotic pressure between the external and internal part of the pellet i.e. the decrease of the chemical potential of grafted acid groups arising from the dilution and solvatation effects that accompany the intake of polar molecules from the fluid phase contacted with the catalyst.

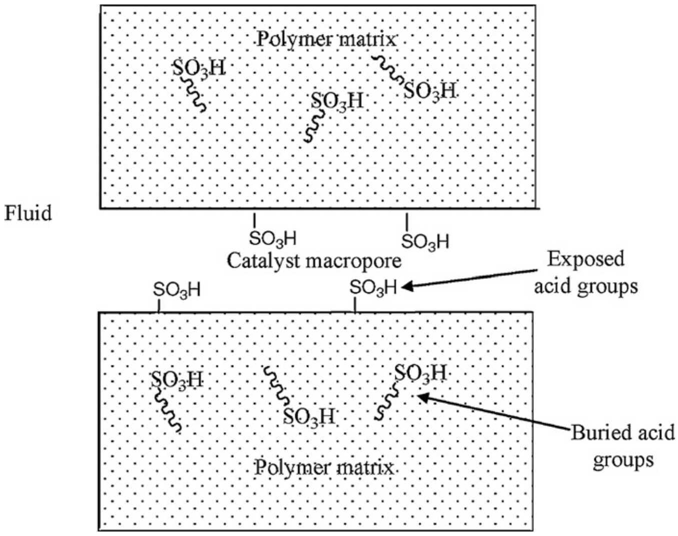

Fig. 2. Schematic representation of a macroporous sulfonic acid resin catalyst.

Additionally, we must consider that high pressure carbon dioxide exhibits a significant solubility in amorphous polymers and in the case of poly(styrene) a value of about 6% (w/w) was measured at 140 °C and 12 MPa using a pressure decaying method [39]. The dissolved gas induces a volume expansion of the polymer that was measured to be close to 7% at 110 °C and 11 MPa [40] and it was estimated, by the Sanchez-Lacombe EOS, to be about 6% at 150 °C and 12 MPa [41].

The effect of CO_2 sorption is then a modification of the polymer from the glassy to the rubbery state that increases by several orders of magnitude the values of diffusivity of molecules inside the matrix [42]. It must be underlined that in the case of poly(styrene) homopolymer the effect should be negligible at the temperature adopted in the transesterification since the polymer should be already in the rubber state (the glass transition temperature T_g of polystyrene being close to 100 °C [43]) but the presence of divinylbenzene crosslinks significantly increases the T_g value [44] so that CO_2 plasticization can play an important role in the acceleration of mass transfer rate of reactants inside the bulk of the matrix.

With this premise it could be possible that the swelling of the polymeric catalyst operated by CO_2 makes accessible to the reactants acidic sites buried inside catalyst particles that usually remain unavailable for catalysis in conventional reaction systems.

It must be underlined that additional phenomena can be considered to explain the enhancement of the yields. One could be an increase of the methanol solubility in the oil phase since mixing the alcohol with CO_2 leads to a marked decrease of the polarity of the binary phase [29]. Also adsorption equilibria of methanol, glycerol and triglycerides on the catalyst surface could be changed by the modified solvent power of the expanded liquid phase.

One other reason could be the acceleration of the mass transfer rates induced by the lower viscosity of the oil phase expanded by CO_2. To study this possibility we repeated experiment 5 in Table 6 in the absence of agitation and decreasing reaction time at 2 h. Quite interestingly, differently from the stirred systems in which the two heaviest phases merged within 40 min from the beginning of the reaction, the three phases remained always distinct even if the intermediate one became yellow coloured with intensity increasing with time. In spite of this clear segregation FAME yields were only slightly depressed changing from 51.9 to 43.6 thus suggesting that also in the presence of the phase boundary and in the absence of mechanical stirring methanol transport in the oil rich phase is quite fast.

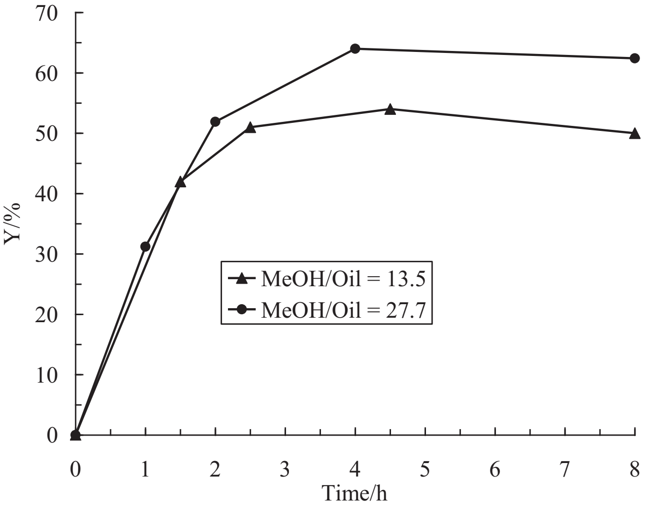

Fig. 3. Plot of FAME yields as a function of reaction time in CO_2 assisted transesterification of rapeseed oil at 140 °C with Purolite CT275 DR (10%, w/w with respect to the oil) at different MeOH/oil molar ratios, oil 8.7 g, nominal density 0.44–0.45 g/mL, pressure 10.8–11.0 MPa. The lines are merely a guide for the eyes.

Anyway at the current state of the research we have not enough elements to discriminate clearly among the importance of these different phenomena in the modification of the performances.

3.4. Transesterification reactions in two fluid phase systems: effect of reaction time

Under adopted operative conditions, the best performances of the transesterification reaction were obtained working at 140 °C with a MeOH/oil molar ratio of 27.7 and nominal density of about 0.44 g/mL (Exp. 5, Table 6). Then we decided to study the kinetics of the process at these operative conditions decreasing the reaction time at 4, 2 and 1 h.

The obtained FAME yields are plotted as a function of the reaction time in Fig. 3 (circles). Most of the methyl esters were formed during the first 2 h. At longer time we observed a gradual decrease of the rate of formation of FAME that became negligible after 4 h. Final FAME yield reached a value of about 65%.

An important parameter in the transesterification of vegetable oils is the alcohol to oil ratio. In traditional liquid systems high values of this ratio allowed the operators to improve significantly the performances of the process [22,24]. To study the effect of this parameter in two fluid phase systems expanded with CO_2 we performed a set of experiments with different reaction times decreasing the loaded mass of methanol at fixed total quantity of vegetable oil thus generating a MeOH/oil molar ratio of 13.5. An additional amount of CO_2 was delivered to the cell in substitution of part of the unloaded methanol. Under adopted conditions, it seemed that the rate of the transesterifcation was not affected by the depression of the methanol concentration during the first 2 h (triangles in Fig. 3). On the other hand, FAME yields reached a final value close to 50% that was lower than that obtained with the higher MeOH/Oil ratio thus suggesting that, also in the presence of CO_2, the adoption of higher alcohol/oil ratios is beneficial in two fluid phase systems.

A possible explanation of the asymptotic trend of FAME yields could be the deactivation of the acid catalyst that can be attributed to several phenomena. One is the desolfonation of the resin that could be accelerated by the adoption of a reaction temperature close to the maximum allowable for the catalyst operation.

To check this possibility we performed a control experiment using the same catalyst of experiment 5 in Table 6. The test was carried out for 2 h and a lower acid resin concentration was reached owing to incomplete recovery of the catalyst from the previous run. Before its reutilization the resin was washed three times with methanol (10 mL each washing). Results are reported in Table 7 together with the outcomes of an experiment carried out for the same time with fresh catalyst. After the treatment, the FAME yield reached a value that is one third of that obtained with the fresh catalyst at the same experimental conditions. Anyway the activity of recycled Purolite was roughly 50% than that of the fresh catalyst if comparison is made in terms of average turn over frequencies TOF (mmol/meq h) defined by the equation

$$\mathrm{TOF} = 3\,\frac{10 Y W^{0}_{\mathrm{oil}}}{\mathrm{PM}_{\mathrm{oil}}(\mathrm{DWC}) M_{\mathrm{cat}} t} \qquad (2)$$

where Y is the FAME yield (%), $W^0{}_{\mathrm{oil}}$ and $\mathrm{PM}_{\mathrm{oil}}$ are the initial mass (g) and the average molecular weight (g/mol) of adopted rapeseed oil respectively, DWC and M_{cat} are the dry wet capacity (meq/g) and the mass (g) of the adopted acid resin respectively and t is the reaction time (h).

These results clearly indicate that a complete desolfonation did not occur and other reasons must be invoked to explain the observed catalyst deactivation. An additional effect depressing the catalytic activity during the reaction could be the preferential adsorption on the acidic sites of glycerol coproduced during the transesterification. This hypothesis is supported by the fact that acid resins are quite effective in the removal of free glycerol from raw FAME streams thus avoiding the utilization of water washing of the biodiesel [45]. Methanol washing could be effective in removing at least partially the adsorbed glycerol thus allowing the partial restoration of the catalytic activity. This hypothesis could be coherent with the observed trend of final FAME yield as a function of MeOH/oil ratio. In fact higher MeOH concentration could confer to the CO_2 rich phase an higher solvent power towards glycerol that could be separated more effectively from the catalyst particles.

3.5. Transesterification reactions in two fluid phase systems: comparison of different polymeric acid catalysts

Some experiments were performed also to compare the activity of different polymeric acid resins in the CO_2 assisted transesterification of rapeseed oil (Table 8).

When the CT275DR catalyst was compared with CT169DR, a different commercial styrene-divynilbenzene acid resin from Purolite, we observed a decrease in the FAME yields from 52 to 33% that corresponded to an apparent decrease of the average TOF from 1.70 to 1.20.

Table 7
Acid resin catalyzed transesterification of rapeseed oil assisted by $scCO_2$ in two fluid phase systems: effect of catalyst recycle.

Exp.	CT275DR (%, w/w)[a]	P^0 (MPa)	Time (h)	TOF (mmol/meq h)	Y (%)
1	Fresh 10	11.0	2	1.71	51.9
2	Recycled 8	11.0	2	0.75	17.2

[a] Catalyst loading % (w/w) with respect to the oil, rapeseed oil 8.6–8.7 g, MeOH/oil = 27.7 mol/mol, ρ = 0.44–0.45 g/mL, T = 140 °C. TOF, average turn over frequency (Eq. (2)).

Table 8
Heterogeneously catalyzed transesterification of rapeseed oil assisted by $scCO_2$ in two fluid phase systems: comparison among different polymeric acid resins.

Entry	Catalyst	Time (h)	T (°C)	P^0 (MPa)	Oil (g)	MeOH/oil (mol/mol)	ρ (g/mL)	TOF (mmol/meq h)	Y (%)
1	CT275DR	2	140	10.9	8.71	27.7	0.45	1.70	51.9
2	CT169DR	2	140	11.0	8.64	27.7	0.44	1.20	33.3
3	CT275DR	8	120	9.7	8.64	27.7	0.44	1.11	45.6
4	SAC-13	8	120	12.6	8.63	27.7	0.44	2.20	6.9

T, reaction temperature; P^0, initial pressure; ρ, nominal density; TOF, average turn over frequency; Y, yield in methyl esters. Catalyst loading 10% w/w with respect to the oil.

As there is no reason to think that single acid site activity is significantly altered in the two different resins, this result could be considered an indirect evidence supporting the role in the process of the acid sites buried in the matrix. In fact the main differences between the two catalysts (Table 1) are a lower DWC and slightly smaller pore diameters that are anyway large enough to make improbable the hypothesis that the kinetic control shifts towards internal mass transfer.

A lower degree of sulfonation is usually associated to a lower penetration of the functionalization in the bulk of the matrix, then the decrease in the value of average TOF could be an indication that a lower concentration of inner sites is available for the reaction.

To investigate the effect of the nature of the polymer matrix we compared the behaviour of Purolite CT275DR with that of Nafion® SAC-13 (see entries 3 and 4 in Table 8). Nafion® is the trade name of a copolymer derived from tetrafluoroethylene and perfluoro-2-(fluorosulfonylethoxy)propyl vinylether, which after hydrolysis of the sulfonyl fluoride, yields the strongly acidic terminal $CF_2CF_2SO_3H$ group [46]. Since we are dealing with a bulk polymer, in the perspective of catalytic applications, an important drawback is the very low surface area that significantly depresses apparent catalytic activity. To overcome this drawback Nafion® resin silica nanocomposite has been developed, where nanometer sized perfluorinated resin particles (5–30 nm average diameter) are entrapped within a highly porous silica network. By this approach a material with properties quite similar to those of a macroporous styrene-divynilbenzene resin is obtained [47].

In comparison with the latter, SAC-13 is then characterized by a significant higher specific area and a much lower acid sites concentration (Table 1). The lower DWC should be at least partially compensated by the higher acid strength of the sites.

Experiments were carried out at 120 °C and after 8 h FAME yields reached with Purolite were almost sevenfold that obtained with the perfluorinated resin. On the other hand, when the catalysts were compared in term of average TOF, the Nafion acid sites were found, as expected, significantly more active than the sulphonic groups of the hydrocarbon resin. This result suggests that, under adopted conditions, the transesterification reaction is more sensitive to the higher concentration of acidic sites of styrene-based materials than to the stronger acidity of perfluorinated resin sulfonic catalysts.

4. Conclusions

The methanolysis of rapeseed oil over commercial styrene-divinylbenzene macroporous acid resins as catalysts was studied in a batch reactor in the presence of supercritical carbon dioxide at $T = 100–140$ °C and $P = 10–46$ MPa.

To obtain high enough yields of fatty acid methyl esters it was necessary to work at reaction temperatures higher than 120 °C. The supercritical component induced an enhancement effect on the kinetics of the transesterification since when CO_2 was added to the reaction system methyl ester yields were almost doubled. This acceleration was already observed at the lowest investigated operating pressure working in a two-fluid phase system. Further amplification of the operating pressure up to 38–46 MPa allowed the two fluid phases to merge in a single one but it did not change significantly the performances of the process.

Experiments performed changing the reaction time indicated that most of the esters were formed during the first two hours, the FAME yield becoming constant at reaction times higher than 4 h. This stationary value increased when higher values of the MeOH/Oil molar ratio were adopted.

The positive effect of $scCO_2$ on the transesterification kinetics could be attributed to its swelling power towards the amorphous polymer matrix that significantly increases diffusion coefficient of reactants in the bulk of the catalyst making accessible sulfonic acid sites buried inside it. Anyway CO_2 can affect the kinetic behaviour of the system also enhancing the solubility of the alcohol in the oil phase or depressing its local viscosity with consequent intensification of the mass transfer rates.

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