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Double-bond depletion of soybean oil triglycerides with $KMnO_4/H_2O$ in dense carbon dioxide

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Abstract−Soybean oil triglycerides (SOT) can be used for the synthesis of rigid polymers. This research investigates the potential of using dense (sub/supercritical) CO_2 in the reaction medium for the addition of functional groups to SOT. As an alternative and novel method, the reaction of SOT with $KMnO_4$ in the presence of water and dense CO_2 is presented. Dense CO_2 is utilized to bring the soybean oil and aqueous $KMnO_4$ solution into contact. Experiments are done at 10, 25, 34.5, 50 °C and 2.5, 5, 7, 11, 16 MPa. Effects of temperature, pressure, $NaHCO_3$ addition, and $KMnO_4$ amount on the conversion (depletion by bond opening) of soybean-triglyceride double bonds (STDB) are investigated. The highest STDB conversions, about 40%, are obtained at the near-critical conditions of CO_2. The addition of $NaHCO_3$ enhances the conversion; one mole of $NaHCO_3$ per mole of $KMnO_4$ gives the highest benefit. Increasing $KMnO_4$ up to 10% increases the conversion of STDB.

Key words: Sub/Supercritical Carbon Dioxide, Reaction, Soybean Oil, Triglyceride, $KMnO_4$

INTRODUCTION

Oils and fats of vegetable and animal origin offer possibilities for providing chemistry with a wealth of reaction products, which will be of great value in the future. The chemical possibilities of renewable oils and fats are still very far from being fully exploited [Biermann et al., 2000].

Petroleum-based raw materials that are used to synthesize polymers can be replaced by renewable plant-based raw materials, namely vegetable oils. The major drawback of the synthesis of polymers from vegetable oils is that these oils cannot be converted into polymers in their original form. Wool et al. [2000] proposed that by the addition of some functional groups, the vegetable oils could be used as raw material for polymer synthesis. The double bonds of the triglyceride were used to form epoxidized triglyceride, hydroxy-formylated triglyceride, and hydroxylated triglyceride. The maleinized triglyceride was synthesized by the reaction of allylic carbon functionality and the reaction of ester group led to the formation of monoglycerides and hydroxy amids. All of these derivatives are capable of polymerization to rigid polymers [Wool et al., 2000].

The addition of functional groups, such as -OH, to triglycerides can be done with $KMnO_4$ solution if the solubility problem of oil in water can be overcome. Oil can be dissolved in acetone or ethanol and by the help of phase-transfer catalysts, permanganate ions can be carried from water to the organic phase [Morrison and Boyd, 1992]. However, in this case, the separation of solvent from the hydroxylated triglyceride is a problem.

In order to overcome these problems, the reaction of $KMnO_4$ with the triglyceride can be carried out in an environmentally friendly medium, such as supercritical CO_2 ($scCO_2$), which has considerable solvent power at moderate temperatures and pressures. Supercritical fluids (SCFs) have been proven in the last decade as environmentally benign media for chemical and related topics. Some recent reviews cover the new processes and products that have been developed by capitalizing on the inherent physical and chemical properties of SCFs [Eckert et al., 1996; Brennecke, 1997; Sherman et al., 1998; Marr and Gamse, 2000; Hautal, 2001].

Among more recent applications, SCFs have been employed as reaction media for chemical reactions. As a reaction medium, the SCF may either participate directly in the reaction [Jessop et al., 1996; Karakaş et al., 1997; Poliakoff and George, 1998; Fischer et al., 1999; Wang and Keinzle, 2000; Park et al., 2002; Lee et al., 2005a, b] or simply act as a solvent for the various chemical species [Ikushima et al., 1992, 1996; Ellington et al., 1994; Knutson et al., 1995; Weinstein et al., 1996; Hadida et al., 1997; Renslo et al., 1997; Palo and Erkey, 1998; Gray et al., 1999; Akgerman and Lin, 1999; Arunajatesan et al., 2001; Oliveira and Oliveira, 2001; Rezaei and Temelli, 2001; Park et al., 2001; Nam and Kim, 2004].

There are numerous advantages of using SCFs in chemical synthesis, all of which are based on the unique combination of properties of either the materials themselves or the supercritical state. There are several reviews that explain the benefits of using SCFs as reaction environment [Buback, 1994; Clifford, 1994; Savage et al., 1995; Dinjus et al., 1997; Poliakoff et al., 1997; Wai et al., 1998; Baiker, 1999; Jessop and Leitner, 1999]. According to Savage et al. [1995], conducting chemical reactions at supercritical conditions affords opportunities to manipulate the reaction environment (solvent properties) by manipulating pressure and temperature, enhance the solubilities of reactants and products, eliminate interphase-transport limitations on reaction rates, and integrate reaction and separation operations. Among SCFs, the application of $scCO_2$ as reaction medium for chemical synthesis has received considerable attention [Ikushima et al., 1992, 1996; Ellington et al., 1994; Weinstein et al., 1996; Hadida et al., 1997; Renslo et al., 1997; Palo and Erkey, 1998; Gray et al., 1999; Akgerman and Lin, 1999; Arunajatesan et al., 2001; Oliveira and Oliveira, 2001; Rezaei and Temelli, 2001; Srinivas and Mukhopadhyay, 1994; Weinstein et al., 1999], since CO_2 is in-

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expensive, relatively nontoxic and nonflammable, poses minimal problems with regard to waste disposal, and the critical temperature and pressure of CO_2 (31.04 °C and 7.38 MPa) can easily be reached.

The major problem of the reaction with $KMnO_4$ solution is that the water-soluble $KMnO_4$ and the water-insoluble substrate must be brought into intimate contact. The focus of our research is to investigate the potential of using $KMnO_4$ and dense CO_2 in the reaction medium for the addition of functional groups, such as -OH, to soybean oil triglycerides (SOT), which can be used for the synthesis of rigid polymers. Dense CO_2 is utilized to bring the soybean oil and aqueous $KMnO_4$ solution into contact by capitalizing on the solvent power of dense CO_2 at moderate temperatures and pressures. Thus, the above-mentioned problems associated with the reaction with $KMnO_4$ via classical means, such as the use of a phase-transfer catalyst and solvent removal are eliminated. Three scenarios to reveal mechanisms of the reaction are discussed:

i) reaction occurs in the aqueous phase
ii) reaction occurs in the dense gas phase
iii) reaction occurs at the interface of the aqueous and dense gas phases

These scenarios are supported by the solubility of CO_2 in H_2O and H_2O in CO_2. In this work, as an alternative and novel method, we will present the reaction of the SOT with $KMnO_4$ in the presence of water and dense CO_2.

EXPERIMENTAL

1. The Setup

The schematic diagram of the experimental set-up is depicted in Fig. 1 [Aydoğan, 2001]. It consists of a high-pressure cell, which has a three-valve sampling system, immersed in a constant temperature water bath. For the agitation of the cell contents, a magnetic stirrer is used. The temperature of the bath is kept within ±0.1 °C by a thermostat (Heto CB7) for experiments done at and above 25 °C. The refrigerated bath at −25 °C and a thermostat (Heto CB7) are used to maintain the temperature of the bath within ±0.1 °C for experiments done below 25 °C. A water/monoethylene-glycol mixture is circulated through a copper coil immersed in the bath in order to decrease the temperature of the water bath to 10 °C.

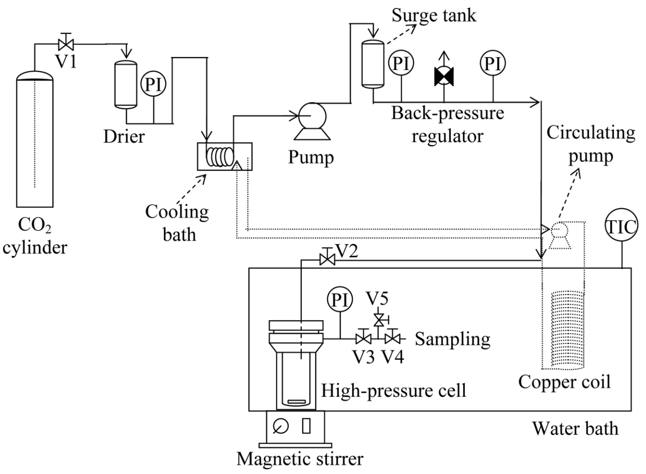

Fig. 1. The experimental set-up.
PI: Pressure Indicator V: On-off Valve
TIC: Temperature Indicator Controller

CO_2 is supplied to the cell at a pressure of 6 MPa at 15 °C from a gas cylinder with a dip-tube attachment. The on-off valve V1 enables the CO_2 flow to the system. The water vapor that might be present in the commercial grade CO_2 is removed by a drier (silica gel bed, 6.15 cm ID and 25 cm length). The gas is then cooled to −10 °C in the refrigerated bath containing water/monoethylene-glycol mixture so that the vapor pressure of CO_2 is kept below the atmospheric pressure and probable gasification is prevented before entering the diaphragm pump (Lewa, type EK). Liquid CO_2 is then pumped to the desired operating pressure by the diaphragm pump, the head of which is also cooled by the circulated refrigerant. The diaphragm pump is capable of compressing the gas up to 40 MPa, and the pressure gauge placed after the pump outlet allows the monitoring of the pressure.

Pressurized CO_2 is introduced into a locally manufactured surge tank (6.15 cm ID and 25 cm length) to dampen the fluctuations generated by the operation pump. In order to maintain a constant pressure within the system, a hand adjustable back-pressure regulator with an accuracy of ±1% of the relief pressure range (Tescom Co. Series 26-1700, model 26-1724-24) is used.

The effective volume of the cell (reactor) is 230 mL (12 cm height, 6 cm ID, 8 cm OD). The cell, which was manufactured from 316 SS, is a bolted-type high-pressure cell. The cell is sealed with a Teflon gasket installed between the head and the main part of the vessel. The pressure in the cell is measured with a pressure gauge (0-25 MPa) (Badotherm Instruments, Holland).

CO_2 is pumped to the cell via the inlet valve V2 (Swagelok Co., 1/4 in ID, two-way ball valve) on the head part of the cell. The sampling line and the valve system are on the main part of the cell. The valve system consists of three valves V3, V4 and V5 (Swagelok Co., 1/4 in ID, two-way ball valves) that are connected to each other with the stainless steel tubing (1/4 in) and a T-junction (1/4 in). Valve V4 is used to release the pressure within the cell while valve V5 is used to clean the system while keeping V3 closed for isolation of the valve system from the vessel.

2. Procedure

In the experiments (Table 1), a predetermined amount of $KMnO_4$ (including $NaHCO_3$ for some experiments) was dissolved in distilled water. This solution, along with a predetermined amount of soybean oil (Table 1), was put into the cell, which was then immersed into the constant-temperature water bath.

After the specified temperature and pressure were attained in the cell, the magnetic stirrer was switched on. The contents of the cell were mixed according to the predetermined period, and after this period, the stirrer was switched off. A one-hour period was required in order to allow the contents inside the cell to settle down. After this period, the valves V2 and V4 were opened and the exiting gas was bubbled in distilled water in order to discharge the pressure inside the cell and to capture the reaction products. The sampling line was then washed with distilled water (40 mL) and then with diethyl ether (40 mL) in order to obtain the residues inside the pipeline. Subsequently, the residue in the cell was collected in a flask. Finally, the samples obtained and the residue collected in the flask were mixed. This allowed the final sample to contain both the un-

Table 1. The experimental program

Run	Temperature (°C)	Pressure (MPa)	Soybean oil wt%	$KMnO_4$ wt%	Water wt%	$NaHCO_3$ wt%	% Conversion of STDB
1	50	16	23.5	0.0	76.5	0.0	0.2
2	10	16	21.0	10.7	68.3	0.0	9.7
3	10	11	21.0	10.7	68.3	0.0	12.8
3R	10	11	21.0	10.7	68.3	0.0	15.1
4	10	7	21.0	10.7	68.3	0.0	6.5
5	10	16	19.9	10.1	64.7	5.3	13.3
6	10	11	19.9	10.1	64.7	5.3	17.8
7	25	16	21.0	10.7	68.3	0.0	21.4
7R	25	16	21.0	10.7	68.3	0.0	20.8
8	25	11	21.0	10.7	68.3	0.0	19.1
8R	25	11	21.0	10.7	68.3	0.0	17.9
9	25	7	21.0	10.7	68.3	0.0	31.7
9R	25	7	21.0	10.7	68.3	0.0	34.0
10	25	5	21.0	10.7	68.3	0.0	11.9
11	25	16	19.9	10.1	64.7	5.3	24.4
11R	25	16	19.9	10.1	64.7	5.3	29.1
12	34.5	16	21.0	10.7	68.3	0.0	27.1
13	34.5	11	21.0	10.7	68.3	0.0	24.0
14	34.5	7	21.0	10.7	68.3	0.0	14.5
15	34.5	16	20.4	10.4	66.5	2.7	26.7
16	34.5	16	19.9	10.1	64.7	5.3	35.0
17	34.5	16	18.8	9.6	61.4	10.2	35.6
18	50	16	21.0	10.7	68.3	0.0	36.3
19	50	11	21.0	10.7	68.3	0.0	34.6
20	50	7	21.0	10.7	68.3	0.0	17.8
20R	50	7	21.0	10.7	68.3	0.0	20.8
21	50	2.5	21.0	10.7	68.3	0.0	22.5
22*	25	7	21.0	10.7	68.3	0.0	37.9
23	25	7	19.0	19.3	61.8	0.0	34.0
24	25	7	22.2	5.6	72.2	0.0	25.3

R: Replicate runs, wt: weight, *: 24-hour reaction period

reacted and reacted components in the CO_2 phase, in the lines, and in the cell, so that the entire system can be considered as a batch system.

The sample was filtered after adding diethyl-ether (250 mL) and waiting for five minutes in order to allow the organic components to enter the diethyl-ether phase. The filtered sample was placed into the phase separator. A five-hour period was necessary in order for the distilled water and diethyl-ether phases to be separated. The diethyl-ether phase (the upper phase) was taken to a flask. Na_2SO_4 was added to the flask in order to remove the water that could be present in the sample. The sample was filtered again and the diethyl-ether phase was collected in an evaporating dish. Then, diethyl-ether was evaporated and the remaining organic components were recovered. The samples obtained from the experiments were analyzed by NMR spectrometry (Varian T-60A NMR spectrometer).

3. Materials

The materials used for this study were commercial soybean oil (Soyola), technical grade $KMnO_4$ and analytical grade $NaHCO_3$. The soybean oil, $KMnO_4$, $NaHCO_3$, diethyl ether (anhydrous, J.T. Baker), and Na_2SO_4 (anhydrous grade for analysis, Merck) were used as received. CO_2 (99.7% pure) was supplied in cylinders equipped with dip tubes by "Habaş Inc." (İstanbul, Turkey).

RESULTS AND DISCUSSION

In this work, 30 experiments, including 6 experiments to check the reproducibility, were performed at 10, 25, 34.5, 50 °C and 2.5, 5, 7, 11 and 16 MPa. The experiments were performed as given in Table 1. The weight %'s given in the table were calculated by excluding CO_2. The replicate runs are indicated with "R". Soybean oil, $KMnO_4$, and water amounts were kept constant except for runs 1, 23, and 24. Run 1 was carried out in order to check if $KMnO_4$ was responsible for the reaction. Runs 23 and 24 were done to explore the effect of the concentration of $KMnO_4$ on the conversion of the reaction. The reaction period was kept constant at 12 hours for all experiments except for run 22, which was 24 hours. The effect of $NaHCO_3$ addition on conversion of the reaction was explored in runs 5, 6, 11, 11R, 15, 16, and 17.

The samples were examined by proton NMR. To analyze the results quantitatively, % conversion (depletion) of STDB was calculated. The integration of the olefin proton peaks was used to determine the amount of C=C present in the sample taken from the experiment. The glycerol peak was integrated to give the amount of glycerol in the sample. Since the glycerol part of the oil is not affected by the reaction, the conversion of STDB was obtained by comparing the ratio of the integration results of C=C and glycerol peaks of the sample taken after the reaction with the same ratio of the integration results of unreacted soybean oil. The % conversion of STDB is given as,

$$\%\ \text{Conversiton of STDB} = \left(1 - \frac{D_S/G_S}{D_O/G_O}\right) \times 100$$

where D_S/G_S represents the ratio of the integration results of C=C and glycerol peaks of the sample taken after the reaction, and D_O/G_O represents the ratio of the integration results of C=C and glycerol peaks of unreacted soybean oil.

Cocero et al. [2000] suggested that the presence of oxygen in high purity CO_2 could cause the degradation of an unsaturated compound. Since one of the reactants is soybean oil, which is an unsaturated compound, an experiment (Run 1) was carried out as a blank test. This test showed that the soybean oil double bonds were not oxidized with the oxygen present (between 0.022 and 0.033 weight%) in the CO_2. Also, this experiment was done to test if $KMnO_4$ was responsible for the opening of the double bonds of the soybean oil. The weight percent of soybean oil and water was 23.5% and 76.5%, respectively. The reaction temperature was 50 °C and the system pressure was 16 MPa. The reaction period was 12 hours. The conversion of STDB was 0.2%, from which it was concluded that $KMnO_4$ was responsible for the decrease in the double bonds of the soybean oil throughout the experiments.

The conversion of STDB changed from 6.5% at 10 °C and 7 MPa to the 36.3% at 50 °C and 16 MPa for the experiments without $NaHCO_3$. These results are promising, since the conversion of STDB is zero without the presence of CO_2 in the reaction environment. This reveals that the presence of the dense gas phase provides the necessary environment for the reaction.

The reaction mixture is a multiphase system, an organic phase containing soybean oil and CO_2, an aqueous phase with CO_2 and $KMnO_4$ ($NaHCO_3$ for some experiments) and a dense gas phase in which soybean oil and water dissolve. Therefore, it is not easy to comment on where the reaction takes place and the effects of pressure, temperature, $KMnO_4$ and $NaHCO_3$ concentrations on the conversion of STDB. The reaction may occur in the aqueous phase, in the dense gas phase or at the interface of the dense CO_2 and aqueous phase.

As the first scenario, if it is assumed that the reaction of soybean oil with $KMnO_4$ and water in the presence of dense CO_2 takes place in the aqueous phase, which consists of $KMnO_4$ and dissolved CO_2, then the reaction must be controlled by the mass transfer of the soybean oil either from the organic phase or from the dense gas phase to the aqueous phase. However, soybean oil is not soluble in water under normal conditions.

Phiong et al. [2003] reported that the use of $scCO_2$ as a reaction solvent in the three-phase catalytic hydrogenation of α-methylstyrene significantly increases the rate of reaction by modification of phase equilibria, in particular, by an increase in the solubility of H_2 in the liquid phase. They concluded that the increase in the solubility of the H_2 in the liquid phase is due to the volumetric expansion of the liquid phase with CO_2. It is well known that the CO_2 is soluble in water [Wiebe, 1941; Wiebe and Gaddy, 1940] and soybean oil [Tegetmeier et al., 2000]. Tegermeir et al. [2000] found that the volume increases up to 6% for water and up to about 45% for corn oil, whose composition is similar to the composition of soybean oil, due to the solvation of CO_2. Therefore, it is possible that the expanded volume leads to lower viscosities and higher diffusivities, which enhances the solubility of soybean oil in water and increases the rate of reaction between the soybean oil and aqueous $KMnO_4$ and consequently increases the conversion of STDB.

The change in the solubility of CO_2 in water [Wiebe, 1941] with temperature is given in Fig. 2(a-c). It can be seen from Fig. 2(a-c) that as the temperature increases at constant pressure, the solubility of CO_2 decreases in water. The volume expansion of water is proportional to the solubility of CO_2 in water [Tegetmeier et al., 2000]. Therefore, if the reaction occurs in the aqueous phase, at constant pressure the conversion of STDB must decrease with increasing temperature.

The effect of temperature on % conversion of STDB with temperature can be seen in Fig. 3(a-c). The experiments were carried out at four different temperatures: 10, 25, 34.5 and 50 °C, at pressures of 7, 11 and 16 MPa. The amounts of soybean oil, $KMnO_4$ and water were kept constant in all experiments at 21, 10.7 and 68.3

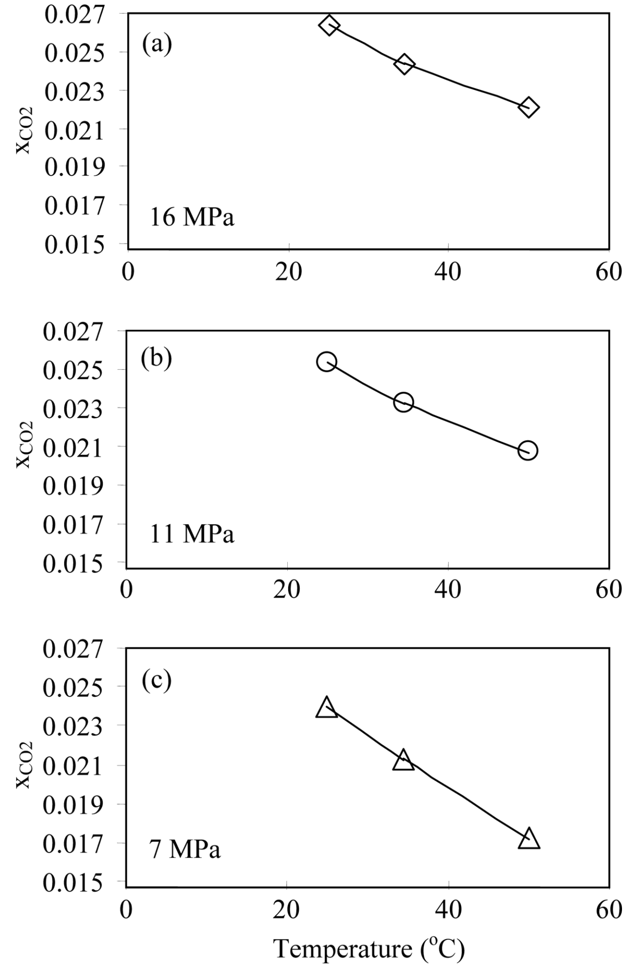

Fig. 2. The change in the solubility of CO_2 in water with temperature at 16, 11 and 7 MPa [Wiebe, 1941].

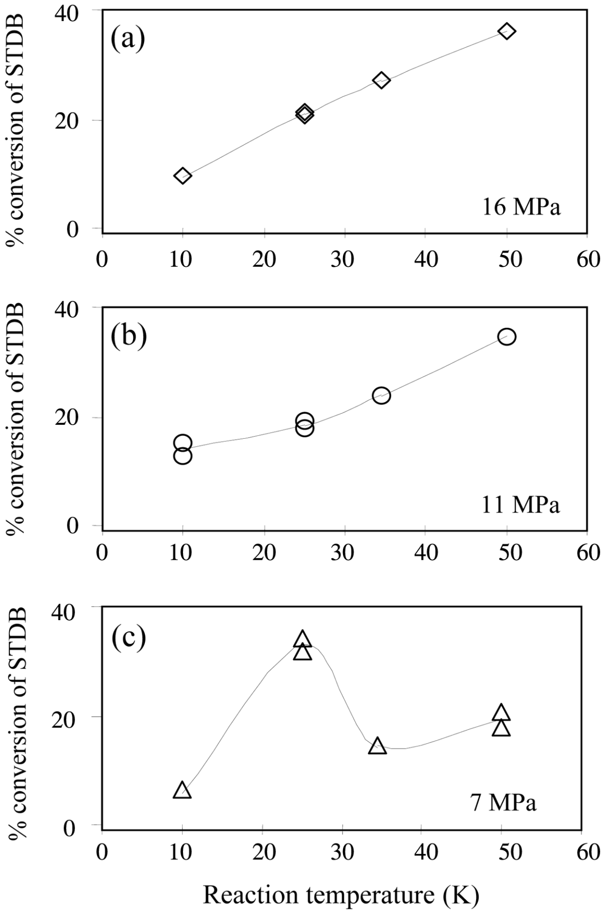

Fig. 3. Effect of reaction temperature on the % conversion of STDB at 16, 11 and 7 MPa.

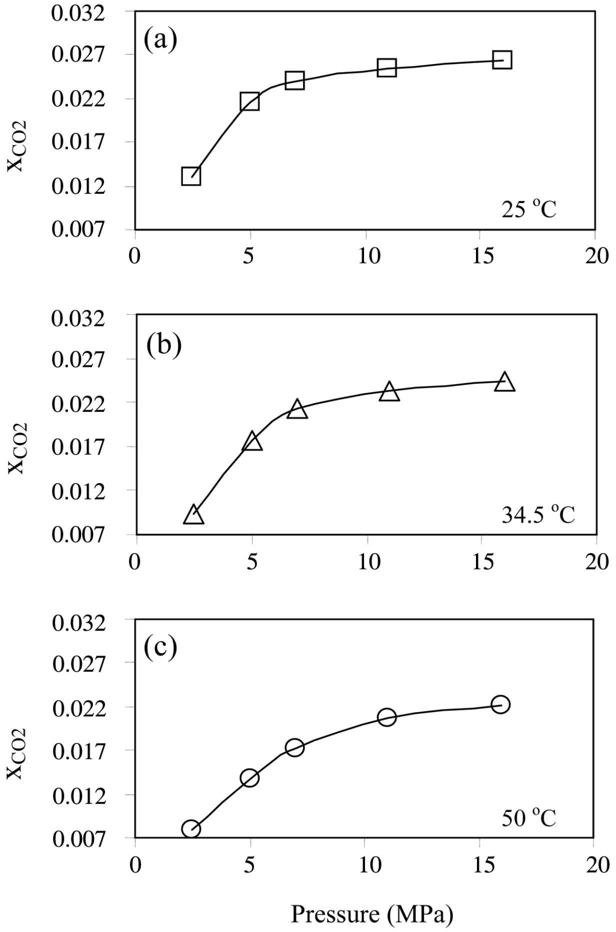

Fig. 4. The change in with pressure at 25, 34.5 and 50 °C [Wiebe, 1941].

weight%, respectively. The reaction period was 12 hours. Fig. 3(a-b) shows that, at constant pressure, the increase in temperature leads to an increase in the % conversion of STDB. It can be observed from Fig. 3(c) that, at 7 MPa, the conversion of STDB increases significantly when the temperature is increased from 10 to 25 °C, and then decreases with further increase in temperature to 34.5 °C, and then again increases with the increase in temperature to 50 °C. However, if the experimental condition of 25 °C and 7 MPa is excluded (which is quite close to the critical point of pure CO_2 and must be treated separately), it can be clearly seen that the conversion of STDB increases with temperature. This does not agree with our first scenario that the reaction takes place in the aqueous phase. However, the reason for this behavior can be the increase in the rate coefficient of the reaction with increasing temperature.

Fig. 4(a-c) shows the effect of pressure on the solubility of CO_2 in water [Wiebe, 1941] at constant temperature. According to Fig. 4(a-c), the solubility of CO_2 in water increases with increasing pressure, from which it can be concluded that the % conversion of STDB must show a similar behavior if the reaction occurs in the aqueous phase.

The change in % conversion of STDB with pressure is shown in Fig. 5(a-d). In order to investigate the effect of pressure on the % conversion of STDB, the experiments were carried out at 2.5, 5, 7, 11 and 16 MPa pressures, at temperatures of 10, 25, 34.5 and 50 °C. The amounts of soybean oil, $KMnO_4$ and water were kept constant during the experiments at 21, 10.7 and 68.3 weight%, respectively. The reaction period was kept constant at 12 hours.

As it can be observed from Fig. 5(a), at 10 °C, the results suggest that the conversion of STDB increases initially when the pressure is increased from 7 to 11 MPa and then decreases with further increase of the pressure to 16 MPa. At 10 °C, the CO_2 is liquid at the pressures studied. The reaction between CO_2 and water leads to the formation of solid carbon dioxide hexahydrate at this temperature [Wiebe and Gaddy, 1940]. The formation of solid carbon dioxide hexahydrate, as an additional phase, may affect the course of the reaction and therefore, it becomes very difficult to decide on the effect of pressure on the conversion of STDB at this temperature.

Fig. 5(b) shows the effect of pressure on the conversion of STDB at 25 °C. If the result of the experiment at 7 MPa is excluded (which is quite close to the critical point of pure CO_2 and must be treated separately) the increasing trend of the conversion of STDB with increasing pressure can be seen clearly. Experimental results obtained at 34.5 °C are given in Fig. 5(c). It can be seen from Fig. 5(c) that as the system pressure increases, the conversion of STDB also increases. In Fig. 5(d), the effect of pressure on the conversion of STDB at 50 °C is presented. As observed from Fig. 5(d), the conversion of STDB initially decreases when the pressure is increased from 2.5 to 7 MPa and then gradually increases with the increase in pressure

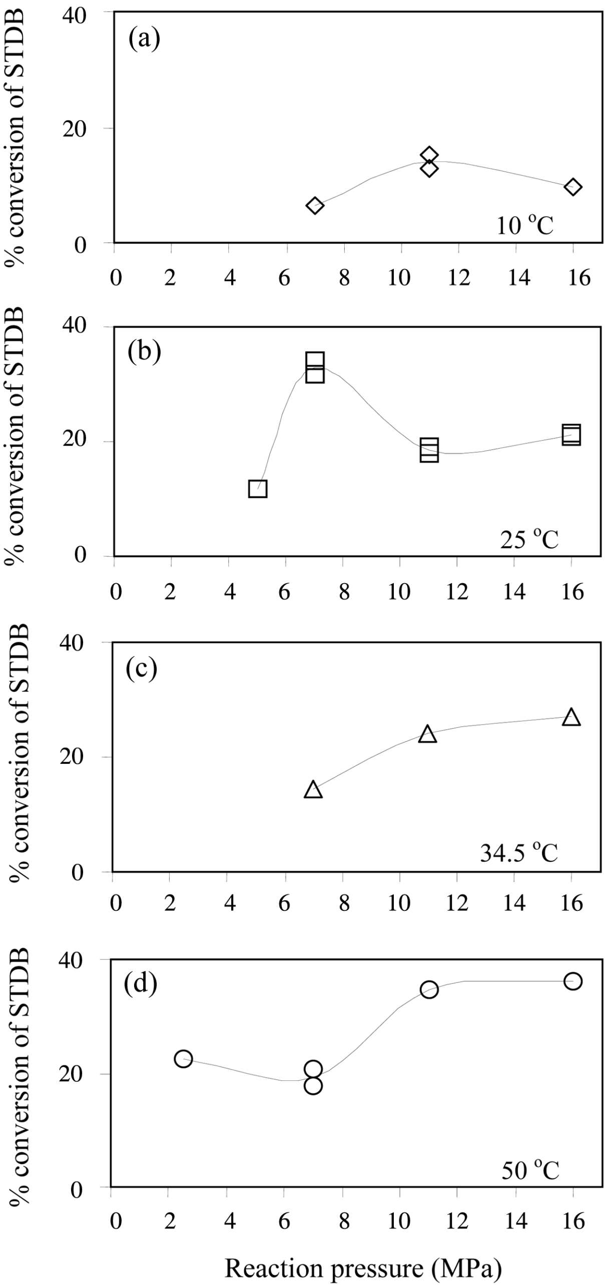

Fig. 5. Effect of reaction pressure on % conversion of STDB at 10, 25, 34.5 and 50 °C.

to 11 and 16 MPa. It can be seen that the behavior of conversion of STDB and x_{CO_2} with pressure is similar by comparing Figs. 5(b-d) and 4(a-c) except for the decrease in % conversion of STDB with an increase in pressure from 2.5 to 7 MPa at 50 °C and if the experimental condition of 25 °C and 7 MPa is excluded. Considering the temperature and pressure effects, the first scenario is not very conclusive.

As the second scenario, it may be suggested that the reaction takes place in the dense gas phase, which dissolves soybean oil and water. In this case, the solubilities of water in dense CO_2 and soybean oil are the key features that will affect the % conversion of STDB. The most important and doubtful assumption of this scenario is that the solubility of $KMnO_4$, which is not soluble in dense CO_2 alone, is dependent on the solubility of water in dense gas phase.

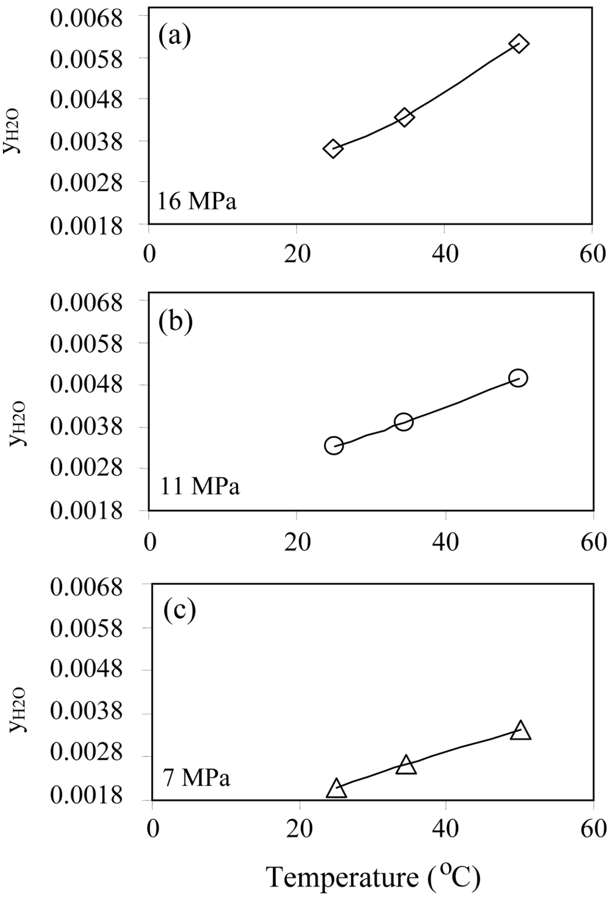

Fig. 6. Effect of temperature on the solubility of water in the dense CO_2 at 16, 11 and 7 MPa [Wiebe, 1941].

Fig. 6(a-c) shows the effect of temperature on the solubility of water in CO_2 [Wiebe, 1941] at 16, 11 and 7 MPa. The solubility of water in dense CO_2 is enhanced by the increase in the temperature at constant pressure. Hence, as the dense CO_2 dissolves more water at higher temperatures, the amount of $KMnO_4$, which is soluble in water, may increase in the dense-gas phase (according to our assumption). This situation must lead to higher conversions of STDB with increasing temperature at constant pressure, which is the case as can be seen from Fig. 3(a-c) (if the experimental condition of 25 °C and 7 MPa is excluded). However, at constant pressure, the solubility of soybean oil decreases with increasing temperature in the low-pressure region below 30 MPa because the density of CO_2 decreases at higher temperatures. However, it can be observed from Fig. 7(a-b) that as the density of pure CO_2 decreases, an increase in the % conversion of STDB occurs. This behavior of STDB conversion conflicts with the second scenario, which assumes that the reaction is carried at the dense phase.

The solubility of soybean oil in dense CO_2 is enhanced with pressure at 25 °C, 34.5 °C and 50 °C [Stahl et al., 1988; Eggers, 1985]. The effect of pressure on the solubility of water in dense CO_2 [Wiebe, 1941] is given in Fig. 8(a-c). It can be seen that the solubility of water also increases with increasing pressure at the pressures studied. Also, the behavior of conversion of STDB and y_{H_2O} with pressure is similar by comparing Figs. 5(b-d) and 8(a-c) (if the experimental con-

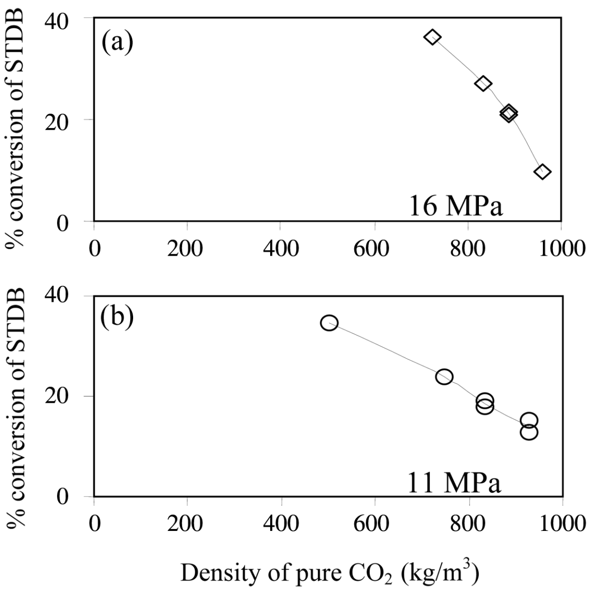

Fig. 7. The change in % conversion of STDB with density of pure CO_2 at 16 and 11 MPa.

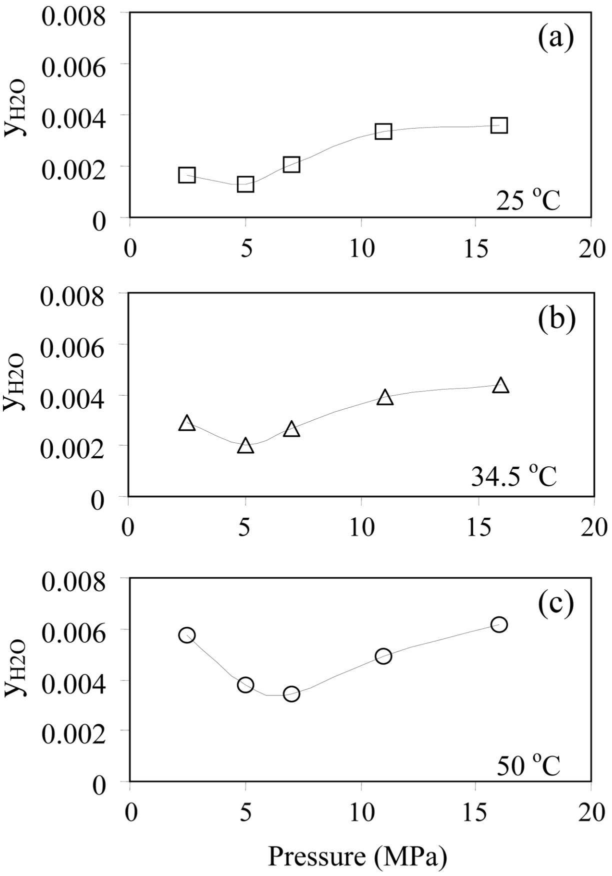

Fig. 8. Effect of pressure on the solubility of water in the dense CO_2 at 25, 34.5 and 50 °C [Wiebe, 1941].

dition of 25 °C and 7 MPa is excluded). This supports the second scenario that the reaction takes place in the dense-gas phase.

The change in the conversion of STDB with the change in pure

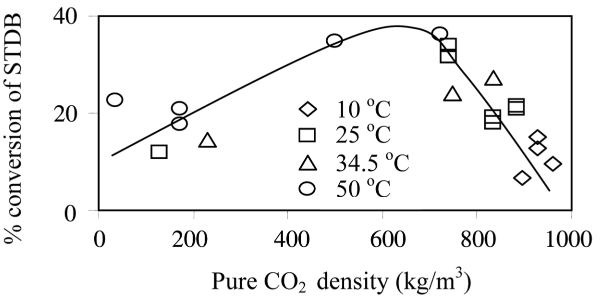

Fig. 9. The change in the conversion of STDB with the change in pure CO_2 density.

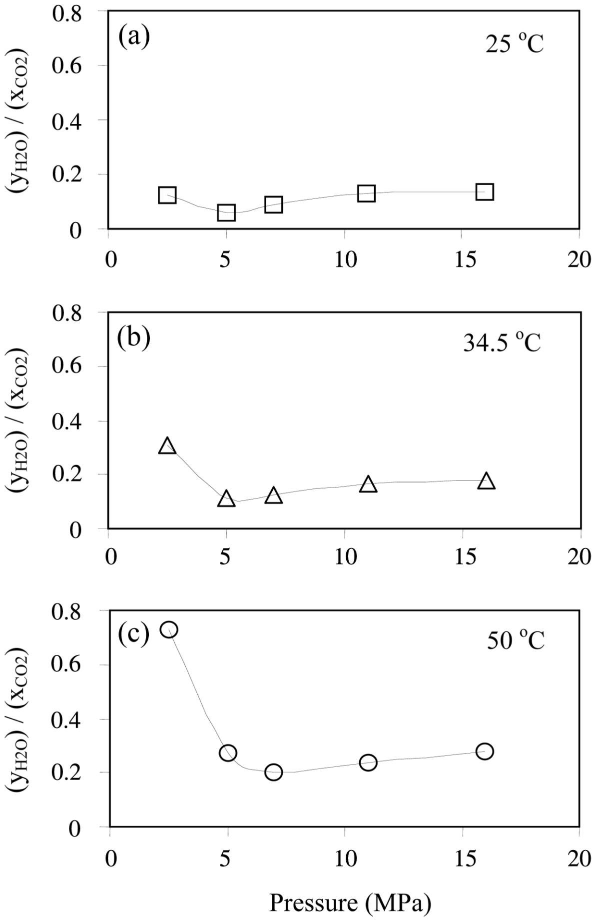

Fig. 10. The change of the ratio of solubility of water in CO_2 to solubility of CO_2 in water with pressure at 25, 34.5 and 50 °C [Wiebe, 1941].

CO_2 density is shown in Fig. 9. It can be observed that as the density of pure CO_2 increases from a gas-like density to a liquid-like density, the conversion of STDB initially increases from 10.0 to 35.0% up to around 600 kg/m^3 and then decreases to 6.0% when the density reaches around 1,000 kg/m^3. This behavior of conversion suggests that the most favorable experimental conditions for the reaction are those giving pure CO_2 densities of around 600 kg/m^3, which is close to the pure CO_2 density around the critical region. The dependence of % conversion of STDB on the density of pure CO_2 also supports that the reaction occurs at the dense gas phase.

The changes in the ratio of solubility of water in CO_2 [Wiebe, 1941] to the solubility of CO_2 in water [Wiebe, 1941] (y_{H_2O}/x_{CO_2}) with pressure at 25, 34.5 and 50 °C are given in Fig. 10(a-c), respectively. If (y_{H_2O}/x_{CO_2}) ratio is high, it means that the amount of water dissolved by the CO_2 is high and the amount of CO_2 dissolved in the water is low. It can be seen that, at 25 °C, the behavior of conversion of STDB and (y_{H_2O}/x_{CO_2}) ratio with pressure is similar by comparing Figs. 10(a) and 5(b) (if the experimental condition of 25 °C and 7 MPa is excluded). Also, at 34.5 and 50 °C, similar behavior of conversion of STDB and (y_{H_2O}/x_{CO_2}) ratio can be observed by comparing Fig. 10(b-c) with Fig. 5(c-d), respectively. These results also strengthen the scenario that the reaction occurs in the dense gas phase.

There is a sharp increase in the conversion of STDB at the experimental conditions of 25 °C and 7 MPa, (Figs. 3(c) and 5(b)). If the reaction is assumed to occur in the dense gas phase, this increase may be explained by the transition-state theory and large negative activation volumes near the critical point [Savage et al., 1995]. For CO_2, near its critical point at constant temperature and volume, the pressure decreases with the introduction of a solute because of the attractive forces between the solute and the solvent molecules [Savage et al., 1995]. This intermolecular attraction translates into a very large contraction in volume in order to balance the pressure. This contraction results in the very large negative partial molar volumes of solutes [Eckert et al., 1986]. The activation volume can be very large positive or negative value depending on the relative magnitude of the partial molar volumes of the species involved [Akgerman and Lin, 1999]. If the activation volume is positive, then the reaction is hindered by the pressure, whereas if the activation volume is negative, then the reaction will be enhanced by pressure. The critical point of CO_2 is 7.38 MPa and 31.04 °C. At experimental condition of 25 °C and 7 MPa, partial molar volumes of the reactants, soybean oil, $KMnO_4$ and water, may become very large negative numbers, and this may cause a sharp increase in the conversion of STDB by yielding a very large negative activation volume.

However, it is known that $scCO_2$ is not capable of dissolving inorganic compounds, such as $KMnO_4$, directly. Therefore, it may be impossible for the reaction to occur in the dense CO_2 although all of the data support this. The discussion up to now brings us to the third scenario--that the reaction most probably begins at the interface of the dense gas phase and the aqueous phase, initiated by $KMnO_4$ in the aqueous phase, and continues in the dense gas phase, affected by the amount of water present in the dense gas phase. Nevertheless, all these are doubtful and require more research and information.

1. Effect of $NaHCO_3$ Addition

$NaHCO_3$ is used to make the reaction environment alkaline; since it is known that reaction with $KMnO_4$ yields higher conversions to 1,2-diols if the reaction environment is slightly alkaline at the beginning of the reaction [Morrison and Boyd, 1992].

At 34.5 °C and 16 MPa, three experiments are done with different concentrations of $NaHCO_3$, the effect of which on the conversion of STDB is shown in Fig. 11. As it can be observed from Fig. 11, the conversion of STDB does not change significantly until the concentration of $NaHCO_3$ becomes 5.3 weight%. Lapworth and Mottram [Lapworth and Mottram, 1925] suggested that if one mole (or more) of [-OH] ion is present per mole of $KMnO_4$ in the reaction environment, the formation of 1-2,diols is enhanced. This amount is not achieved until the concentration of $NaHCO_3$ is increased to 5.3 weight%, in the experimental conditions studied. However, further increase of the concentration of $NaHCO_3$ does not alter the conversion, significantly. If the reaction environment were saturated with $NaHCO_3$ when its concentration becomes 5.3 weight%, then further increase in the concentration of $NaHCO_3$ would not change the conversion. Nevertheless, there are no data on the solubility of $NaHCO_3$ in any of the phases under dense CO_2, and further research should be done in order to understand this behavior of conversion with $NaHCO_3$ addition.

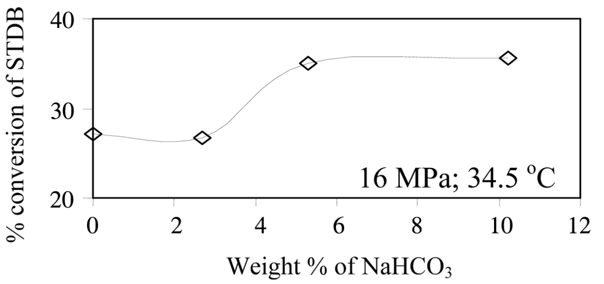

Fig. 11. Effect of $NaHCO_3$ addition on the conversion of STDB at 34.5 °C and 16 MPa.

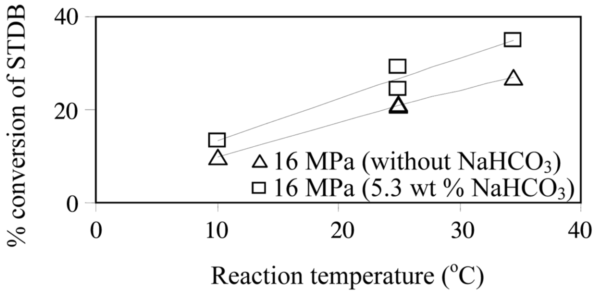

Fig. 12. Comparison of the conversions obtained with and without the addition of $NaHCO_3$ at 16 MPa.

After the optimum concentration of $NaHCO_3$ that should be added to the reaction environment was decided, additional experiments were done to examine if the same effect of $NaHCO_3$ addition was valid for different reactions conditions. Fig. 12 shows the comparison of conversion of STDB obtained without the addition of $NaHCO_3$ with conversion of STDB obtained with the addition of 5.3 weight% $NaHCO_3$ at 10, 25 and 34.5 °C at 16 MPa. It can be observed from Fig. 12 that the conversion of STDB increases with the addition of $NaHCO_3$. At 16 MPa, the temperature dependence of conversion of STDB with and without $NaHCO_3$ addition is similar.

The conversion of STDB is 17.8% for the experimental conditions of 10 °C and 11 MPa when 5.3 weight% $NaHCO_3$ is added to the reaction environment. At 10 °C and 11 MPa, it is possible to say that the conversion is enhanced by the addition of $NaHCO_3$ since conversion of STDB obtained from the experiment without the $NaHCO_3$ addition is 12.8%, with the replicate experiment giving 15.1%.

2. Effect of $KMnO_4$ Concentration

The experiments were carried out with three different concentrations of $KMnO_4$--5.6, 10.7 and 19.3 weight%--at 25 °C and 7 MPa. The reaction period was kept constant at 12 hours. Fig. 13 shows the effect of $KMnO_4$ concentration on the conversion of STDB at 25 °C and 7 MPa. As can be seen, the conversion of STDB initially

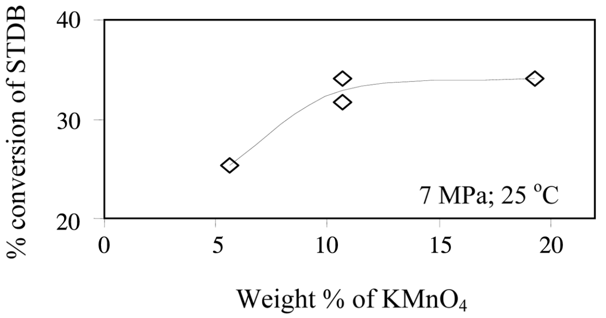

Fig. 13. Effect of $KMnO_4$ concentration on the conversion of STDB at 25 °C and 7 MPa.

increases with the addition of $KMnO_4$, then remains unchanged with further addition of $KMnO_4$.

3. Effect of Reaction Time

The reaction time is kept constant at 12 hours for all experiments except for one. At 25 °C and 7 MPa, if the reaction period is increased to 24 hours from 12 hours, the conversion of STDB increases slightly from 31.7% (replicate being 34.0%) to 37.9%.

CONCLUSIONS

In this work, the potential of using aqueous $KMnO_4$ solution and dense CO_2 as the reaction medium for the addition of functional groups to soybean triglycerides is investigated. Dense CO_2 is utilized to bring the soybean oil and aqueous $KMnO_4$ solution into contact by capitalizing on the solvent power of dense CO_2 at moderate temperatures and pressures.

Three scenarios are discussed to reveal mechanisms of the reaction and supported by the solubility of CO_2 in H_2O, and H_2O in CO_2. According to the first scenario, reaction is assumed to occur in the aqueous phase. However, it is found that this scenario is not conclusive. The second scenario supposes that reaction occurs in the dense gas phase, but it is known that $KMnO_4$ is not soluble in the dense phase. Therefore, it is concluded that the reaction most probably begins at the dense gas phase and the aqueous phase interface, initiated by $KMnO_4$ in the aqueous phase, and continue in the dense gas phase, affected by the amount of water present in the dense gas phase, which is a third scenario.

The highest conversions, around 40%, are obtained at the conditions where the density of CO_2 reaches its near-critical value. The addition of $NaHCO_3$ to the reaction environment, at constant temperature and pressure, enhances the conversion of STDB, if one mole of $NaHCO_3$ is added per mole of $KMnO_4$.

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