

# Polymerizable oil synthesis by hydroxyhalogenation of soybean oil in dense CO<sub>2</sub>

Öznur Saygı<sup>a</sup>, Selim Küsefoğlu<sup>b</sup>, Uğur Akman<sup>a</sup>, Öner Hortaçsu<sup>a,\*</sup>

<sup>a</sup> Department of Chemical Engineering, Boğaziçi University, Bebek 34342, İstanbul, Turkey

<sup>b</sup> Department of Chemistry, Boğaziçi University, Bebek 34342, İstanbul, Turkey

Received 23 August 2004; received in revised form 1 August 2005; accepted 1 November 2005

## Abstract

The aim of this research is to hydroxybrominate and hydroxychlorinate the double bonds of methyl oleate and soybean oil in dense CO<sub>2</sub>. The hydroxychlorination reactions of vegetable oils in dense CO<sub>2</sub> are the first such report in literature. Experiments were performed at the reaction conditions of 8, 25 and 40 °C and 60, 100, 120 and 150 bar. Effects of temperature, pressure, reaction time and the reactant amounts on the extent of reaction are studied. Hydroxybromination and hydroxychlorination reactions are conducted using sodium hypobromite (NaOBr) and sodium hypochlorite (NaOCl) solutions, respectively. The polymerization of the product is performed by urethane formation with toluenediisocyanate at 40 °C. The products were analyzed by NMR and IR spectrometry. Fifty percent consumption of the double bonds was observed in the hydroxybromination reaction of methyl oleate, but no –OH addition was determined. In hydroxychlorination reactions of methyl oleate the consumption of double bonds ranges from 40 to 95%, and the introduction of –OH groups ranges from 14 to 30%. Best yields were observed when the mole ratio of NaOCl to methyl oleate double bonds is 5 to 1. The consumption of soybean triglyceride double bonds, in the hydroxychlorination reactions, are observed to range from 18 to 75% and the formation of –OH groups ranges from 8 to 33%. The highest conversion for one-step hydroxychlorination of soybean is obtained at 25 °C and 120 bar for a reaction time of 6 h, with 10/1 ratio of NaOCl to double bonds. Better results were obtained when the product of the reaction was reintroduced to the reactor and retreated with NaOCl and 75% consumption of double bonds and 33% formation of –OH groups were observed.

© 2005 Elsevier B.V. All rights reserved.

**Keywords:** Dense carbon dioxide; Reaction; Soybean oil; Triglyceride; Hydroxyhalogenation; Polymerization

## 1. Introduction

Vegetable oils and fats constitute an important renewable raw material for the chemical industry. Considerable research effort is directed to extend the range of compounds obtainable from vegetable oils. Some of the commercially important materials, which can be synthesized from vegetable oils, are polymers. For the last 60 years the most frequently used raw material for polymer synthesis has been petroleum. Due to the accelerating depletion of petroleum reserves and increasing cost of petroleum, the replacement of petroleum with renewable resources, such as plant and animal products has gained importance. Vegetable oils are an economical and environmentally friendly alternative to petroleum for biodegradable polymer syntheses. Genetic engi-

neers try to optimize these renewable raw materials by breeding new and more useful plant species. Developing polymer synthesis from vegetable oils, such as soybean oil, provides a chance to synthesize polymers with the desired qualities from a cheap and renewable source.

The major drawback of polymer synthesis from vegetable oils is that vegetable oils, with a few exceptions such as castor oil, cannot be easily converted into polymers in their original form. Reactive functional groups have to be added to the vegetable oils with unsaturated fatty acid components, to be able to utilize them as monomers for polymer synthesis. The hydroxylated, epoxidized or maleinized triglycerides are capable of polymerizing [1,2]. Several studies have been reported in the literature to add a hydroxyl functional group to vegetable oil triglycerides. However, the immiscibility of the oil phase and reactants in the aqueous phase is a serious problem. Different solvents have been used to cope with this problem. However, the organic solvents used cannot be completely removed from the products, and they

\* Corresponding author. Tel.: +90 212 3596434; fax: +90 212 2872460.  
E-mail address: [hortacsu@boun.edu.tr](mailto:hortacsu@boun.edu.tr) (Ö. Hortaçsu).

usually have deterrent effects on polymer quality and cost. For instance, Eren and Küsefoğlu [3] studied the hydroxybromination of methyl oleate, oleic acid and a genetically modified sunflower oil (high oleic), in an acetone/water mixture by a one-step reaction using *N*-bromosuccinimide. They succeeded in hydroxybromination of fatty acid methyl esters and triglycerides. Their product gave new polymers with interesting properties. However, the high cost of the reagent (*N*-bromosuccinimide), makes the reaction unsuitable for industrial usage.

Sub/supercritical (dense) CO<sub>2</sub> is a solvent, which may be used to bring the oil substrate and reactants together in the aqueous phase. Dense CO<sub>2</sub> has properties much unlike those of ordinary fluids which are tunable simply by changing the system pressure and temperature. Supercritical fluid (SCF) based reaction media also offer flexibility for separation processes by reducing or completely eliminating organic solvent usage, higher reaction rates for diffusion controlled reactions and higher conversions. CO<sub>2</sub> as the most popular SCF has the additional benefit of being a natural, unregulated solvent, with low toxicity and high availability, in addition to being relatively cheap.

Aydoğan [4] and Mercangöz [5,6] studied the oxidative hydroxylation of soybean oil triglyceride double bonds with aqueous potassium permanganate solution by bringing the two immiscible phases together with the aid of sub/supercritical CO<sub>2</sub> phase. Aydoğan [4] concluded that the hydroxylation reaction takes place in supercritical CO<sub>2</sub>. Mercangöz [5,6] re-examined this study and succeeded to obtain a polymer from soybean oil by hydroxylation with aqueous potassium permanganate solution under supercritical conditions. However, the missing part of this study was the reaction mechanism of the resulting polymerization. Mercangöz [5,6] stated that this reaction may be explained in the context of air-oxidation polymerization, but it was not a complete explanation. The study of Mercangöz [5,6], for the first time in literature, clearly showed that it is possible to transfer an aqueous, oil-insoluble reactant to an oil substrate phase by utilizing SCF technology, without the aid of phase transfer catalysts, surfactants or complexing agents.

In this study, the hydroxybromination and hydroxychlorination reactions of soybean oil and the methyl oleate under sub/supercritical conditions are carried out. Appropriate reaction conditions (pressure, temperature and reaction time) in dense CO<sub>2</sub> were investigated.

## 2. Experimental

### 2.1. The set-up

The experimental set-up used is depicted in Fig. 1. The reactions were carried out in a high-pressure stainless steel cell. The cell had a three-valve sampling system. The volume of the cell is 230 cm<sup>3</sup>, having 12 cm height, 8 cm o.d. and 6 cm i.d. The cell has a bolted-type head with two inlets. To keep the reactor contents at constant temperature during the reaction, the high-pressure cell was immersed in a constant temperature water bath equipped with a thermostat for all experiments done at and above 25 °C. For experiments below 25 °C, a refrigerated bath was used.

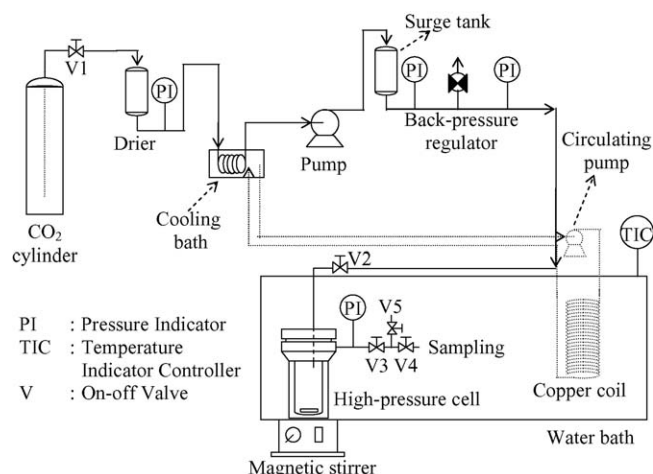


Fig. 1. The experimental set-up.

A pressurized cylinder with a dip-tube attachment was used to supply CO<sub>2</sub> to the system. As seen in Fig. 1, the on-off valve V1 enabled flow of CO<sub>2</sub> to the system. In the experimental set-up, a drier (silica-gel bed, 6.15 cm i.d. and 25 cm length) removed the moisture that might be present in the commercial grade CO<sub>2</sub>. The liquid CO<sub>2</sub> was then cooled to –12.5 °C in the refrigerated bath containing water/ethylene glycol mixture so that the vapor pressure of CO<sub>2</sub> was kept below the atmospheric pressure and probable gasification was prevented before entering the diaphragm pump (Lewa, type EK). Liquid CO<sub>2</sub> was then compressed to the desired operating pressure by the diaphragm pump, the head of which was also cooled by the circulated refrigerant. The diaphragm pump used was capable of compressing the gas up to 400 bar, and the pressure gauge placed after the pump outlet allowed the pressure of the compressed CO<sub>2</sub> to be monitored.

After compression, CO<sub>2</sub> was introduced into a surge tank (6.15 cm inner diameter and 25 cm length) to dampen the fluctuations generated by the pump. In order to maintain a constant pressure within the system, a hand adjustable back-pressure regulator with 1% accuracy of the relief pressure range (Tescom Co.) was used. The regulator was kept slightly open in order to keep the pressure of the compressed gas in the lines at a maximum pressure of 175 bar.

### 2.2. Procedure

The high-pressure cell was charged with the stoichiometrically determined amounts of reactants. The head part was bolted to the cell main body after placing the Teflon-coated magnetic cylinder in the cell. Then the reactor cell was submerged in the constant temperature water bath and connected to the CO<sub>2</sub> line. The reactor cell was placed in line with the magnetic stirrer under the water bath in order to ensure proper mixing. Before charging CO<sub>2</sub>, the cell remained in the water bath for 30 min, to attain thermal equilibrium.

After thermal equilibrium is reached, CO<sub>2</sub> was charged into the system. When the pressure of the cell is in the 30–40 bar range, the inlet valve V2 was closed and valves V3 and V5 were

Download English Version:

<https://daneshyari.com/en/article/232286>

Download Persian Version:

<https://daneshyari.com/article/232286>

[Daneshyari.com](https://daneshyari.com)