Phase-Transfer Catalysed Epoxidation of Soybean Oil Using Hydrogen Peroxide and Supercritical Carbon Dioxide

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Epoxidized vegetable oils are the product of vegetable oil epoxidation reactions. Since the epoxidized vegetable oil is a nonpoisonous plasticizer, it has been wildly used in the plastic packaging of food and medicine. Among the various epoxidized vegetable oils, the application of epoxidized soybean oil is broader than others. Nowadays, it's the third largest category of plasticizers. However, there are serious pollution problems in most of the conventional processes of soybean oil epoxidation.

In this paper, supercritical carbon dioxide and hydrogen peroxide was used in the epoxidation for exploring a clean and efficient process. Supercritical carbon dioxide would be both a solvent and reactant in combination with aqueous hydrogen peroxide, which made the epoxidation be possible through the formation of peroxycarbonic acid as the intermediate oxidizer.

Soybean oil epoxidation was performed in a biphasic system composed of a supercritical CO_2/oil phase and an aqueous H_2O_2 phase. The epoxidation occurred in the aqueous phase. Therefore, the transfer of soybean oil into the aqueous phase is the rate-control step. In order to increase the solubility of soybean oil in the aqueous phase, several phase transfer catalysts was used in this reaction. As shown in Fig.1, adding of $NaHCO_3$ as the stabilizer of H_2O_2 and the phase transfer catalyst, the conversion of soybean oil increased from 1.88 % (without additives) to 12.08 % (with $NaHCO_3$ and SDBS).

The experimental results in directly provided the evidence of the existence of peroxycarbonic acid, and confirmed that peroxycarbonic acid could make soybean oil be epoxidized. The results disclosed that the conversion and yield of the epoxidation in supercritical CO_2 were far more than in gaseous or liquid CO_2 (See Fig.2 and 3).

The highest yield of epoxidized soybean oil was obtained under the reaction conditions as 20h in CO_2 at 40ºC and 15MPa, the molar ratio 1:2.of soybean oil to H_2O_2, the mass ratio 0.05:1 of $NaHCO_3$ to H_2O_2 aqueous solution, and the mass ratio 0.01:1 of phase transfer catalyst to soybean oil.

Being different with the conventional soybean oil epoxidation processes with carboxylic acids as catalysts, in which there are a large amount of carboxylic acids in the epoxidation product and a pollution problem caused by washing the oil product to remove the residual acid, the pH value of the oil product of epoxidation in $ScCO_2$ is 6.7, that means there is nearly no acid in the product and no need to remove the acid by washing. Therefore, the proposed process in this paper could be a more environmentally benign routine for epoxidized soybean oil production.

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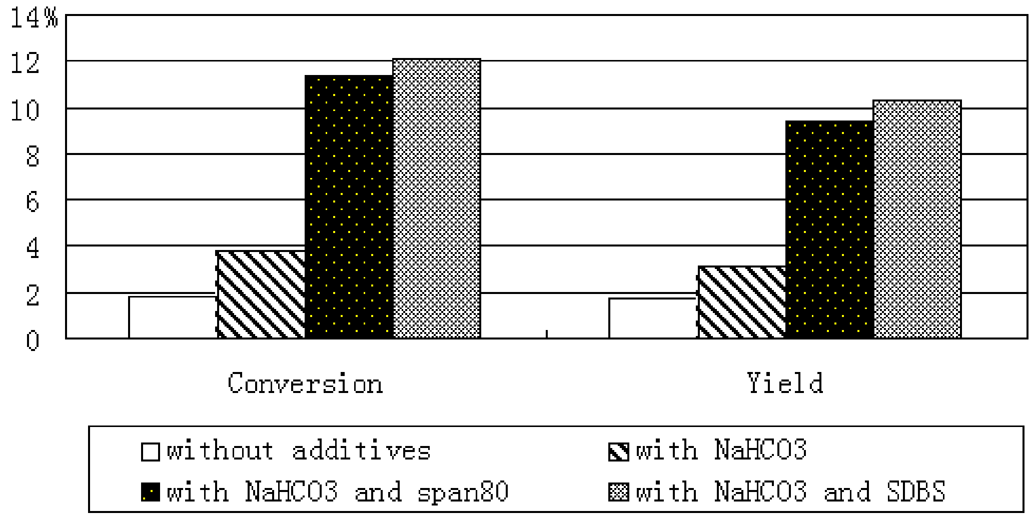

Fig. 1 Soybean oil epoxidation in $ScCO_2$ at 40 ^{o}C and 15 MPa for 20h: the enhancement effect of the phase transfer catalysts and $NaHCO_3$

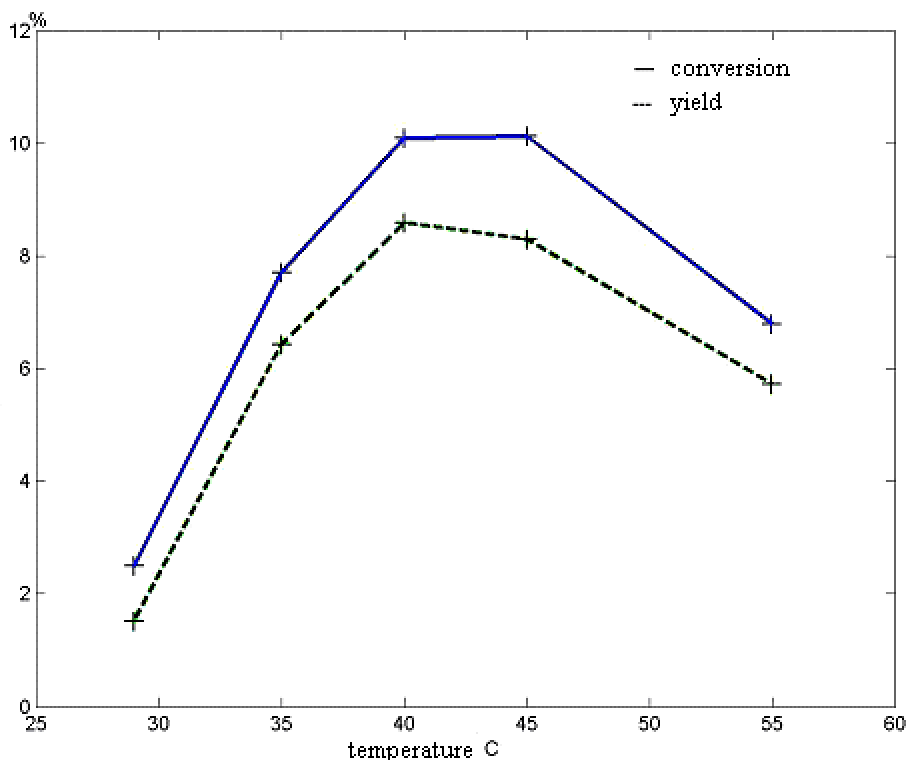

Fig. 2 Effect of reaction temperature on the epoxidation

Reaction was conducted for 12h at 15MPa. The volume ratio of soybean toH_2O_2 solution was 1:1; the mass ratio of $NaHCO_3$ to H_2O_2 solution is 0.05:1; the mass ratio of PEG1000 to soybean oil is 0.01:1.

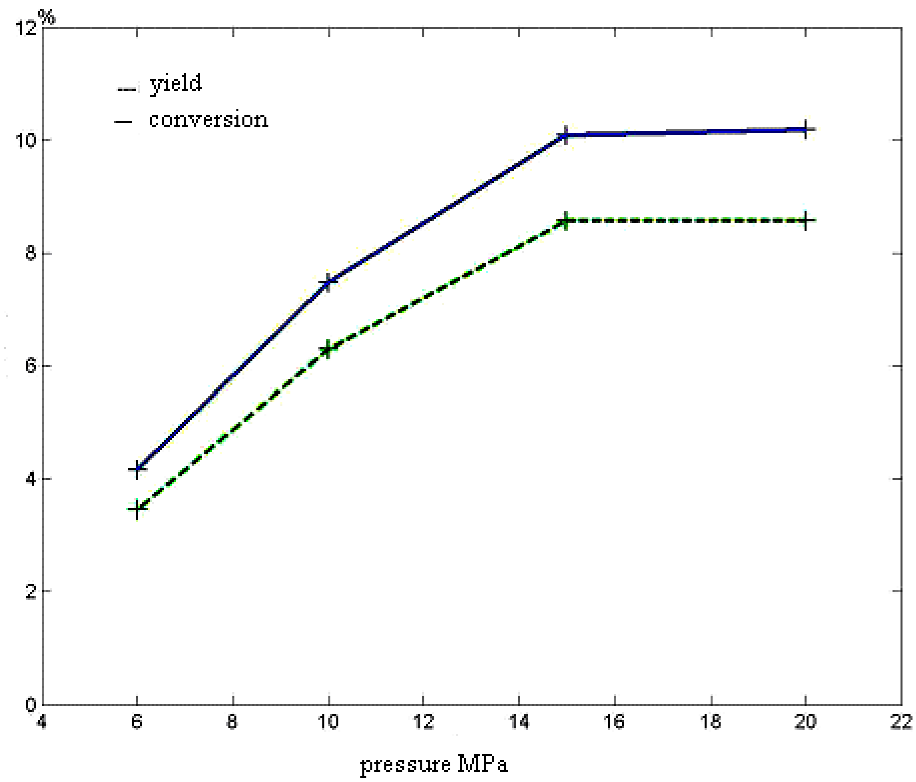

Fig. 3 Effect of reaction pressure on the epoxidation

Reaction was conducted for 12h at 40°C. The volume ratio of soybean toH_2O_2 solution was 1:1; the mass ratio of $NaHCO_3$ to H_2O_2 solution is 0.05:1; the mass ratio of PEG1000 to soybean oil is 0.01:1.