Kinetics of Catalytic Transfer Hydrogenation of Soybean Oil in Microwave and Thermal Field

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The influence of microwave irradiation on the reaction kinetics of the soybean oil catalytic transfer hydrogenation was investigated. The kinetic constants were determined experimentally in a microwave field and are compared with water bath measurements at comparable bulk temperatures. In both the microwave and thermal fields all hydrogenation reactions obey first-order kinetics with respect to the fatty acids. The reaction rates were up to 8 times greater using microwave heating than with conventional heating at the same temperature.

Introduction

The microwave dielectric heating effect uses the ability of some liquids and solids to transform electromagnetic energy into heat and thereby drive chemical reactions. It is well documented that microwave irradiation can be employed to accelerate organic and organometallic reactions,[1–4] solid state syntheses,[5] and polymer syntheses.[6] The bulk of early work on applications of microwave dielectric heating effects on chemical reactions has been reviewed by Mingos *et al.*[7] Other investigators have studied the effect of microwave irradiation on catalytic systems. Wan *et al.*[8,9] developed a technique called "microwave-induced catalysis" which was applied for catalytic conversion of cyclohexene and the decomposition of methane. The large increase of the reaction rate when microwave heating is used is usually attributed to the increase of the reaction temperature.[2,10,15] However, this may not always be the proper explanation as will be demonstrated in our paper.

In the present paper, the influence of microwave radiation on the kinetics of the catalytic transfer hydrogenation (CTH) reactions of soybean oil is reported. The following equation, in which soybean oil component is the acceptor (A) and aqueous alkali formate (sodium formate) dissolved in water is the donor in the presence of Pd on carbon catalysis, represents the CTH process:

$$\mathrm{HCOO^-} + \mathrm{H_2O} + \mathrm{A} \xrightarrow{\mathrm{Pd/C}} \mathrm{AH_2} + \mathrm{HCO_3^-} \qquad (1)$$

This report is strongly connected with our previous work[11] in which the CTH kinetics under conditions of conventional heating was studied in detail. The CTH data for both systems are compared.

Results and Discussion

Soybean oil contains triacylglycerols of saturated fatty acids, palmitic (P) and stearic (S), and unsaturated fatty acids: oleic (Ol), linoleic (L), and linolenic (Le). During the hydrogenation reaction, unsaturated fatty acids compete with the hydrogen donors through adsorption at the "active sites" on the catalyst surface where they are gradually converted to the saturated product.

The general scheme for these reactions may be represented as:[12]

$$\mathrm{Le} \xrightarrow{k_{\mathrm{Le}}} \mathrm{L} \xrightarrow{k_{\mathrm{L}}} \mathrm{Ol} \xrightarrow{k_{\mathrm{Ol}}} \mathrm{S} \qquad (2)$$

It was demonstrated that Bailey's simplified kinetic model[12] for the CTH process with conventional heating could be applied.[11,13] This model assumes that the consecutive reactions are first-order and irreversible and does not discriminate between the isomeric fatty acids. The change of the component concentrations with time is obtained through solution of the following set of equations:

$$\frac{\mathrm{d}C_{\mathrm{Le}}}{\mathrm{d}t} = -k_{\mathrm{Le}}C_{\mathrm{Le}} \qquad (3)$$

$$\frac{\mathrm{d}C_{\mathrm{L}}}{\mathrm{d}t} = -k_{\mathrm{L}}C_{\mathrm{L}} + k_{\mathrm{Le}}C_{\mathrm{Le}} \qquad (4)$$

$$\frac{\mathrm{d}C_{\mathrm{Ol}}}{\mathrm{d}t} = -k_{\mathrm{Ol}}C_{\mathrm{Ol}} + k_{\mathrm{L}}C_{\mathrm{L}} \qquad (5)$$

$$\frac{\mathrm{d}C_{\mathrm{S}}}{\mathrm{d}t} = k_{\mathrm{Ol}}C_{\mathrm{Ol}} \qquad (6)$$

After solution

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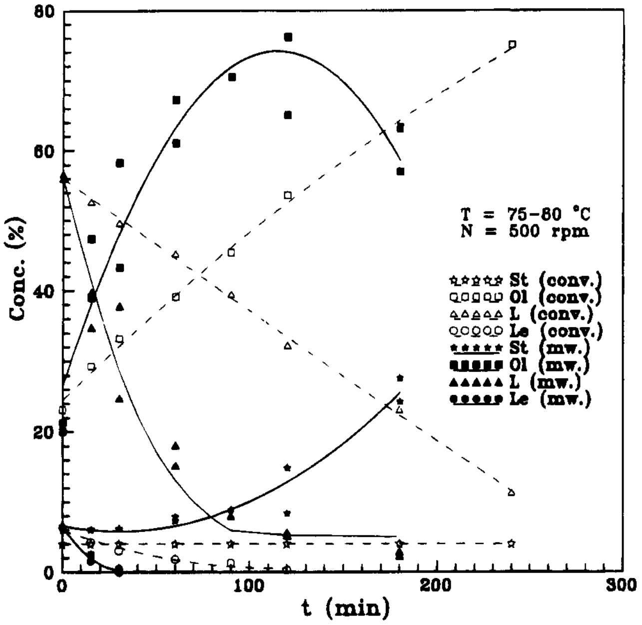

Figure 1. CTH of soybean oil for microwave (75–80 °C) and conventional (80 °C) heating.

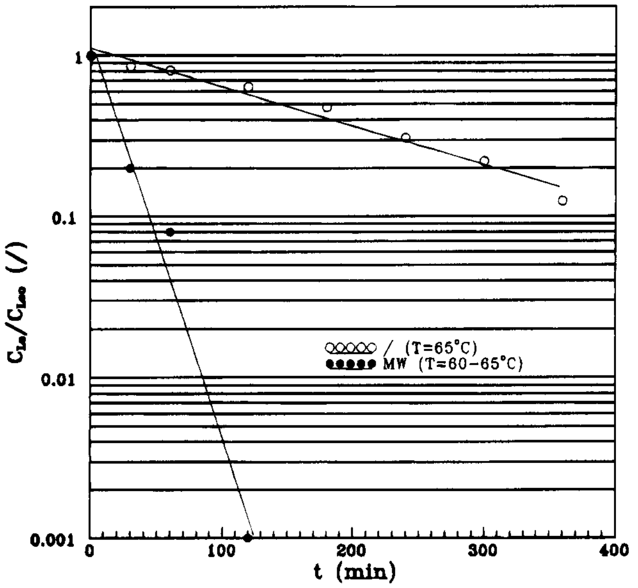

Figure 2. Hydrogenation kinetics of linolenic acid initiated by conventional and microwave heating.

$$C_{Le} = C_{LeO}e^{-k_{Le}t} \tag{7}$$

$$C_L = C_{LO}\left(\frac{k_{Le}}{k_L - k_{Le}}\right)(e^{-k_{Le}t} - e^{-k_Lt}) + C_{LO}e^{-k_Lt} \tag{8}$$

$$C_{Ol} = C_{LeO}\left(\frac{k_{Le}}{k_L - k_{Le}}\right)\left(\frac{k_L}{k_{Ol} - k_{Le}}\right)(e^{-k_{Le}t} - e^{-k_{Ol}t}) - C_{LeO}\left(\frac{k_{Le}}{k_L - k_{Le}}\right)\left(\frac{k_L}{k_{Ol} - k_L}\right)(e^{-k_Lt} - e^{-k_{Ol}t}) + C_{LO}\left(\frac{k_L}{k_{Ol} - k_L}\right)(e^{-k_Lt} - e^{-k_{Ol}t}) + C_{Ol}e^{-k_{Ol}t} \tag{9}$$

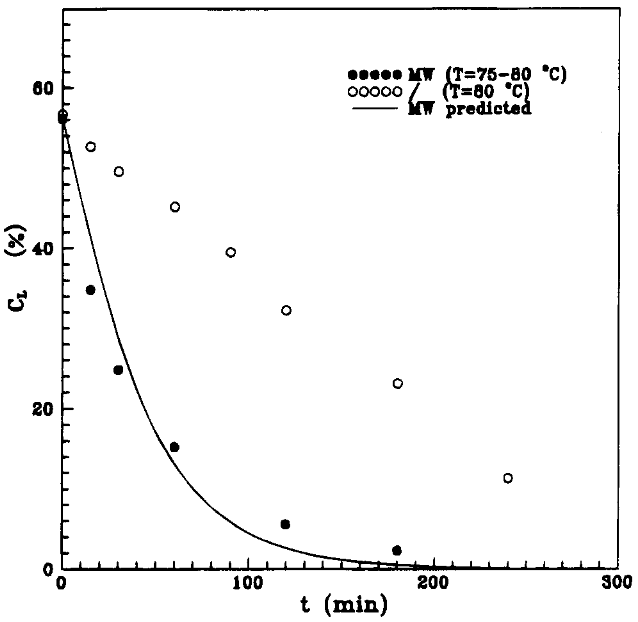

Figure 3. Time course of the linoleic acid concentration for thermal and microwave experiments. Comparison of the experimental data with prediction according to eq 8.

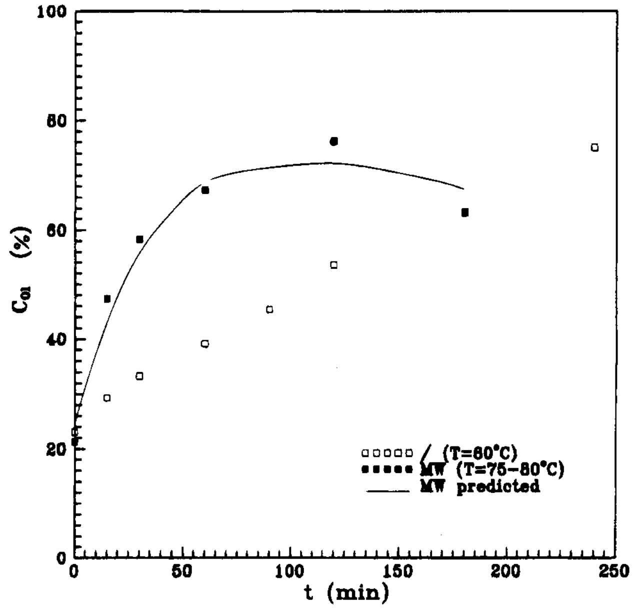

Figure 4. Time course of the oleic acid concentration for thermal and microwave experiments. Comparison of the experimental data with prediction according to eq 9.

where C_{Le}, C_L, C_{Ol} and C_S are the fatty acid concentrations, C_{LeO}, C_{LO}, and C_{OlO} are the initial concentrations, and k_{Le}, k_L, k_{Ol} are the appropriate reaction rate constants. The partial reduction of soybean fatty acids during CTH under microwave and conventional heating is presented in Figure 1. The standard integral method was used to calculate the rate constants for conversion of linolenic acid, k_{Le} (Figure 2). The prediction values of $C_L$and C_{Ol} were calculated numerically from eqs 8 and 9 using the bisection method and C_S values were determined with this stoichiometric equation:

$$C_S = C_{LeO} + C_{LO} + C_{OlO} + C_{SO} - (C_{Le} + C_L + C_{Ol}) \tag{10}$$

Comparison of the experimental data for microwave and conventional heating with predictions using the first-order kinetic model for hydrogenation of linoleic and oleic acid is presented in Figures 3 and 4. It is clearly seen

Table 1. Kinetic Data for the CTH Reactions of Soybean Oil in Sodium Formate Solution under Catalysis of Pd/C with Microwave and Conventional Heating

	temp,[a] °C	k_{Le} (min g)$^{-1}$	k_L (min g)$^{-1}$	k_{Ol}[b] (min g)$^{-1}$
conventional	65	0.012	0.003	0.0001
microwave	60–65	0.095	0.025	0.0027
conventional	80	0.028	0.006	0.0008
microwave	75–80	0.142	0.030	0.0033
conventional	90	0.038	0.008	0.0010

[a] Temperature measurements in bulk between microwave heating periods in experiments in microwave field. [b] All reaction rate constants were calculated on 1 g of Pd/C catalyst.

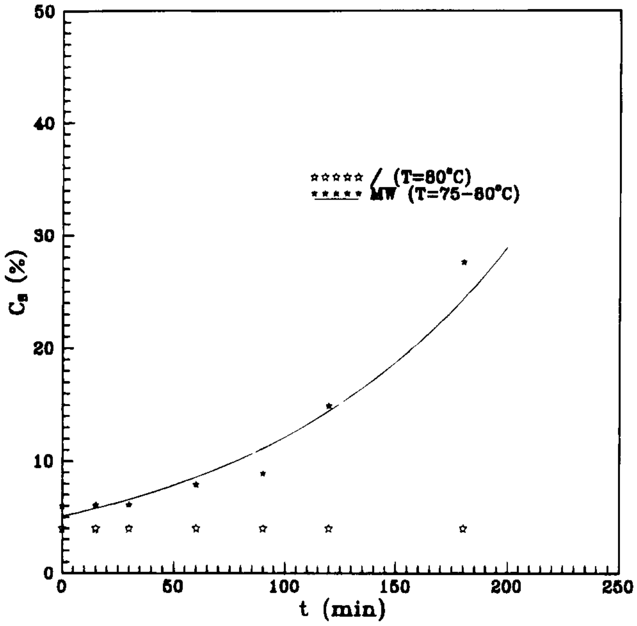

Figure 5. Microwave heating effect on time course of the stearic acid concentration. Comparison of the experimental data with the prediction according to eq 6.

that the fatty acid hydrogenation in microwave and thermal fields is first-order in fatty acid concentrations. Similarly, the selectivity ratio calculated from relationship $S_{Le} = k_{Le}/k_L$ has the value of about 4 in both examples.

However, the hydrogenation reaction rates of fatty acids were about 8 times greater for microwave heating than for conventional heating at comparable temperatures (Table 1). Moreover, an increase of the stearic acid concentration after 60 min from the start of hydrogenation in the microwave field was observed. The concentration of the stearic acid remained constant during the thermal field experiments in the temperature range 65–90 °C (Figures 1 and 5) in the same time period.

The observed increase in the reaction rate cannot be attributed to the increased temperature, as it is usually done[2,10,15] in recent analyses of the microwave-assisted reactions. Rapid mixing of the contents assured the uniformity of the bulk temperature in the laboratory reactor within the prescribed temperature range and hot spots can be excluded. On the other hand, the CTH reactions proceed only at the catalyst surface where donor molecules must be present simultaneously with the unsaturated fatty acids. Only those catalyst particles which are positioned near the oil–water interface can participate in the reaction. It is likely that microwaves can increase the formation of the dynamic oil–water interface as well as the motion of the catalyst particles within the oily drops toward the interface. Furthermore, the exchange of the reactants and products between the catalyst and oil–water solutions may be enhanced through the microwave action. However, there is no direct experimental proof for these effects and the influence of the microwaves on the transport phenomena at the catalyst has to be regarded only as one of the possible explanations. Finally, we would like to emphasize that even though the experiments' repeatability was not completely satisfactory, still the significant effect of the microwaves on the hydrogenation was always observed.

Table 2. Fatty Acid Composition of Soybean Oil and Operating Conditions

fatty acid composition	
$C_{16:0}$ palmitic (P)	9.8%
$C_{18:0}$ stearic (S)	4.0%
$C_{18:1}$ oleic (Ol)	23.1%
$C_{18:2}$ linoleic (L)	56.7%
$C_{18:3}$ linolenic (Le)	6.4%
soybean oil	30 g
donor (NaOOCH)	34 g
water	60 g
catalyst (10% Pd/C)	600 mg
stabilizer (Mayodan M-612)	120 mg
temperature	65–90 °C
agitation	500 rpm

Conclusions

The effect of microwave irradiation on the catalytic transfer hydrogenation of soybean oil using aqueous sodium formate solution as hydrogen donor source and a palladium on carbon catalyst was studied. It has been found that the reaction mechanism is the same as for conventional heating and can be conveniently represented by Bailey's scheme of reactions.[12]

However, a significant increase of the reaction rates at comparable bulk temperatures was observed in the case of the microwave heating. The enhancement of the reaction rate cannot be attributed to temperature and pressure effects as it is usually done in the recent literature. It appears more likely that microwave heating may assist transport processes at the catalyst and oil–water interfaces.

Experimental Section

Materials. Experiments were performed with commercial refined soybean oil from the oil factory HELIOS-Domzale. The sodium formate as hydrogen donor and the 10% Pd/C catalyst were supplied by Fluka, while Mayodan M-612 stabilizer was supplied by Grindsted Co.; all were of the highest purity available.

Experimental Procedures. The kinetics of hydrogenation was investigated at 65 and 80 °C temperature of the reaction mixture in a microwave field and at 65, 80, and 90 °C with conventional heating. In the microwave experiments, weighed amounts of oil, stabilizer, and donor solution (Table 2) were agitated using a mechanical stirrer with a 3 cm round-shaped Teflon blade in a 250 mL round-bottomed flask. Flask was placed in a domestic microwave oven (2450 MHz) which was adapted to allow direct mechanical stirring of the reactants and periodic temperature measurement with a calibrated NiCr–Ni thermocouple. Catalyst was added when the temperature of interest was reached. The power supply was switched on and off during the experiment in order to prevent

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overheating of the reaction mixture. The heating and cooling periods were alternated in time intervals of a few minutes with the estimated net absorbed microwave power of 10–15 W. The temperature was measured before the microwave heating period and immediately after it. The temperature variation was within limits listed in Table 1. The samples were removed and quenched periodically during the run. All analyses were carried out by gas chromatography.

The hydrogenation experiments with conventional heating were described in detail in our previous report.[11] Reagents and supports were mixed in the same proportions already reported for the microwave heating experiments. In both sets of the experiments the stirrer speed was 500 rpm.

Determination of Fatty Acids. Both processes, in thermal and microwave fields, were monitored by determining the fatty acids (FA) of hydrogenated oil samples with a Varian 3400 gas chromatograph. FA were determined (quantitatively) as fatty acid methyl esters (FAME) prepared by IUPAC method II.D.19.[14]

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