Efficient continuous epoxidation of biodiesel in a microstructured reactor

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Abstract−Efficient continuous epoxidation of biodiesel with peracetic acid generated in situ from hydrogen peroxide and acetic acid was studied in detail in a microstructured reactor. The effects of micromixer type, reaction temperature, catalyst usage, flow rate and residence time were considered. Results show the T-type glass micro-structured reactor (TTGMR) outperforms the interdigital multilamination micromixer. Under the optimized conditions, the final product from TTGMR has an epoxy value of 6.5 and an iodine value of 2.2.

Keywords: Epoxidation, Fatty Acid Methylesters, Biodiesel, Microreactor, Liquid-liquid Flow
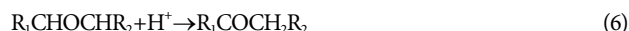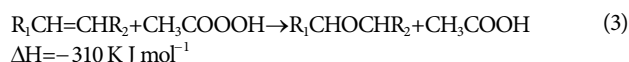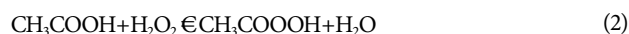
INTRODUCTION

Biodiesel (fatty acid methyl esters, FAMEs) is produced from a chemical reaction of grease, extracted from animal fats, catering waste oils, vegetable oils or aquatic plants, with an alcohol such as methanol. Epoxy FAMEs (EFAMEs), major products from FAMEs, have become increasingly important in the chemical industry because of their availability from highly renewable resources. EFAMEs can be used as the precursors of lubricants, cosmetics and other chemicals, or as plasticizers and polymer stabilizers instead of dioctyl phthalate (DOP) to form products with better physical properties and longer aging time [1]. For example, polyvinyl chloride (PVC) would decompose to form HCl under heat or light, which accelerates the breakdown of chain links and thus leads to the early crack of products. However, EFAMEs can capture HCl by their epoxy groups in plastics and rubber products (Reaction (1)), and then endow the plastics and rubber with thermal stability. EFAMEs can also be used as surfactants and dispersants in epoxy coatings and epoxy production, or as intermediates in the production of polyurethane polios [2]. The application of EFAMEs in the chemical industry improves not only the comprehensive utilization but also the economic benefits of biodiesel [3,4].

$$HCl+R_1CHOCHR_2 \rightarrow R_1CH(OH)CHClR_2 \qquad (1)$$

EFAMEs are usually produced from reactions of acetic acid/formic acid with H_2O_2 (Reactions 2 and 3) [5]. These exothermic reactions mainly proceed in peracid conditions [5-7], which have several drawbacks. For example, the acid-catalysis doxirane ring opening will reduce the selectivity of deoxidized products, and the separation of acidic by-products is difficult. Furthermore, high-temperature reactions will involve unstable intermediate reactants (e.g., peroxide products) and partial EFAME decomposition (Reactions 4-8) [5]. Although there are some high-yield and high-selectivity

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techniques for preparation of EFAMEs in solvents, their industrial applications are limited by the high costs of raw materials [8,9]. The chemical enzyme system was also used to produce high yield of EFAMEs [10]. The reaction substrate was critical for the peroxygenase enzyme, which is specific for epoxidation. Obviously, a rapid and efficient production mode is required for epoxidation of FAMEs.

Microstructured reactors (microreactors) with excellent heat and mass transfer rates afford efficient mixing and precise temperature control for exothermic reactions [11-17], and allow continuous operation. Microreactors have obvious advantages for some reactions, such as Michael addition of amines to α, β-unsaturated carbonyl compounds [18], Moffatt-Swern oxidation [19], and degradation of polybrominated diphenylethers [20]. In this work, the epoxidation of FAME with peracetic acid generated in situ was carried out in a T-type glass microreactor (TTGMR) in comparison to other microreactors. The effects of some reaction parameters on the iodine value (I_V) and epoxy value (Oe) of epoxidation were investigated.

$$CH_3COOH+H_2O_2 \rightleftharpoons CH_3COOOH+H_2O \qquad (2)$$

$$R_1CH=CHR_2+CH_3COOOH \rightarrow R_1CHOCHR_2+CH_3COOH \qquad (3)$$
$$\Delta H=-310\,K\,J\,mol^{-1}$$

$$R_1CHOCHR_2+CH_3COOH \rightarrow R_1CH(OH)CH(OCOCH_3)R_2 \qquad (4)$$

$$R_1CHOCHR_2+H_2O \rightarrow R_1CH(OH)CH(OH)R_2 \qquad (5)$$

$$R_1CHOCHR_2+H^+ \rightarrow R_1COCH_2R_2 \qquad (6)$$

$$R_1CHOCHR_2+CH_3COOOH \rightarrow R_1CH(OH)CH(OOCHOCH_3)R_2 \quad (7)$$

$$R_1CHOCHR_2+H_2O_2 \rightarrow R_1CH(OH)CH(OOH)R_2 \qquad (8)$$

MATERIALS AND METHODS

1. Chemicals and Materials

FAME (acid value: X=0.36 mg KOH/g; density: 0.8598 g/mL) was purchased from Jiangsu Denying Vegetable Oil Plant. Its detailed

Table 1. Composition of FAME raws

Ingredients name	CAS No.	Molar mass (g/mol)	Density (g/mL, 25 °C)	Melting point/boiling point (°C)
Oleate	112-62-9	296.49	0.8739	−19.9/218.5
Linoleic acid methyl ester	112-63-0	294.47	0.8886	−35/215
Stearic acid methyl ester	112-61-8	298.50	0.8498	39.1/215
Methyl palmitate	112-39-0	270.45	0.852	34/185
Anti-oil methyl ester	2462-84-2	296.49	0.871	9.5/

composition (Table 1) was detected by a gas chromatograph (GC) assembled with a flame ionization detector, an Ultra-Alloy HT1 column, and Agilent 6890N. Acetic acid (HAc), 40 wt% H_2O_2, concentrated H_2SO_4 and ethylene diamine tetraacetic acid disodium (EDTA-2Na) were supplied by Shanghai Ling Feng Chemical. The instruments used here included a poly(tetrafluoroethylene) (PTFE) delay loop (i.d. 1.0 mm, length 10 m, Beijing Xiongchuan), high-performance liquid chromatograph (HPLC) pumps (Beijing Chuang Xin Tong Heng Science & Technology Corporation), an high-pressure interdigital multilamination micromixer (HPIMM) (channel width 40 μm, height 37 μm, stainless steel, IMM, Germany) and a T-mixer (width 50 μm, height 50 μm, Microglas, Germany).

2. Experimental Processes

Appropriate molar ratios of concentrated H_2SO_4 (catalyst) and EDTA-2Na (stabilizer of epoxy product) were dissolved in the mixture of HAc and H_2O_2. Then a mixed solution and FAME were pumped into the microreactor assembled with HPIMM and PTFE capillary delay loop (marked as HD) or T-mixer connected with PTFE capillary (TTGMR) or only HPIMM (Fig. 1). The residence time in the delay loop was adjusted by changing the delay loop length. The peroxide reaction of HAc with H_2O_2, and epoxidation of FAME with the resulting peracetic acid proceeded almost simultaneously in the microreactor. The whole microreactor was put into thermostat 1 (Fig. 1) to control the reaction temperature. The export of the delay loop was immersed into an ice-water bath (thermostat 2, Fig. 1) to terminate the reaction. The mixture product was put into an oil-water separator [21]. The lower water phase was separated and then neutralized with deionized water, while the upper oil phase was neutralized to pH 7 with 1 M $NaHCO_3$. The oil phase was then purified by evaporation to remove the low-boiling-point impurities for analysis. After drying, EFAME was obtained.
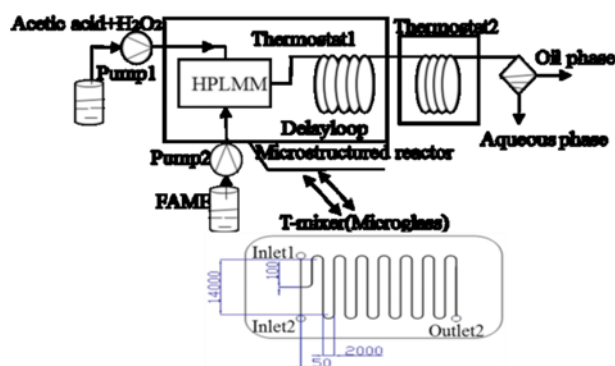
Fig. 1. The experimental setup for production of EFAME in a microreactor.

During the epoxidation, metal ions such as Na^+, Fe^{3+}, Cu^{2+}, Mg^{2+} and Ca^{2+} might have significant effects. EDTA-2Na was chosen as an appropriate completing agent to prevent the ring open-loop of EFAME [22], thus improving the system stability, and reducing the reaction time and production costs [11].

3. Analysis Methods

The acid value is defined as the amount of KOH (mg) required to neutralize 1 g of a sample (GB-T-1668-2008). I_V is defined as the mass of iodine (g) consumed by 100 g of a sample (GB/T 5532-2008). I_V is often used to determine the amount of unsaturation in fatty acids. Oe is defined as the oxygen content in 100 g of a sample (GB/T 1677-2008). Oe underlies the determination of product quality and reflects the epoxidation degree of double bond in the molecular structure [11,23].

RESULTS AND DISCUSSION

1. Effect of Reactor Types on Epoxidation

Three types of commercial microreactors, HPIMM, HD and TTGMR, were investigated in the epoxidation of FAME with HAc and H_2O_2. The reaction conditions were all set the same: molar ratio of H_2O_2 to FAME (-C=C-) = 1.2 : 1; HAc/-C=C- molar ratio= 1.0 : 1; temperature 65 °C; 1 wt% EDTA-2Na; dosage of H_2SO_4 (catalyst)=5 wt%; total flow=5 mL/min. Fig. 2(a) shows the effects of micromixer types on the IV and Oe of the resulting products. Clearly, the application of TTGMR results in the highest Oe (6.5) and lowest Iv (2.2) than both HD and HPIMM. The alternation of oil-water phases facilitates the mass transfer and reaction in the small glass micro channel of the T-mixer. The inner wall of the T-mixer squeezes the dispersed phase to form a circulation in the slugs, which is initiated by the shear between the stationary fluid at the capillary inner wall and the slug axis. The mixing in the fluid segments is enhanced, and the solute diffusion across the liquid/ liquid interface is accelerated by the intensified mixing of the fluid motion in the segments. Circulation within the droplet will accelerate the mass transfer of the two-phase mixture. When the fluid flows through the curved channel, severe turbulence generated by the constant squeezing and stretching of the droplet can speed up the two-phase mixing and reaction [24].

At the same reaction conditions, a certain amount of mixture of FAME, catalyst and stabilizer was fed into a three-necked flask equipped with a stirrer, a dropping funnel and a reflux condenser. Then H_2O_2 was gradually dripped from the dropping funnel into the flask at 50 °C. After that, the stirring was continued and the temperature was increased to 65 °C. During the reaction period from 1 to 2 h, Oe increases from 2.1 to 4.3, while Iv decreases from
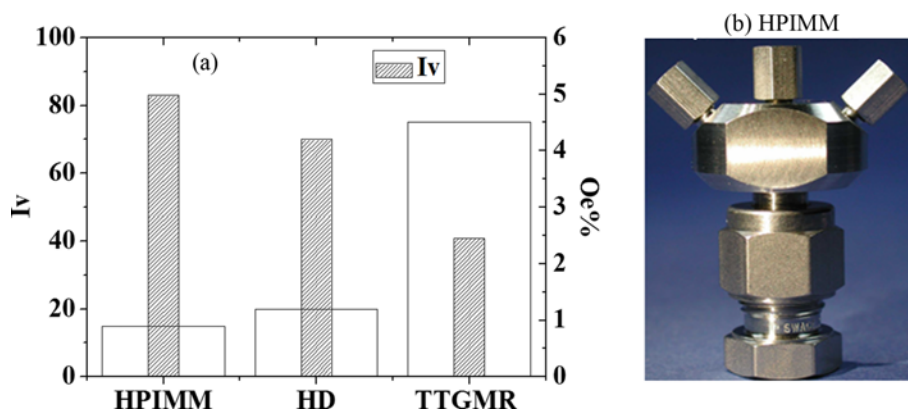
Fig. 2. The Iv and Oe of epoxidation in different reactors, (a) microreactor. (b) HPIMM.
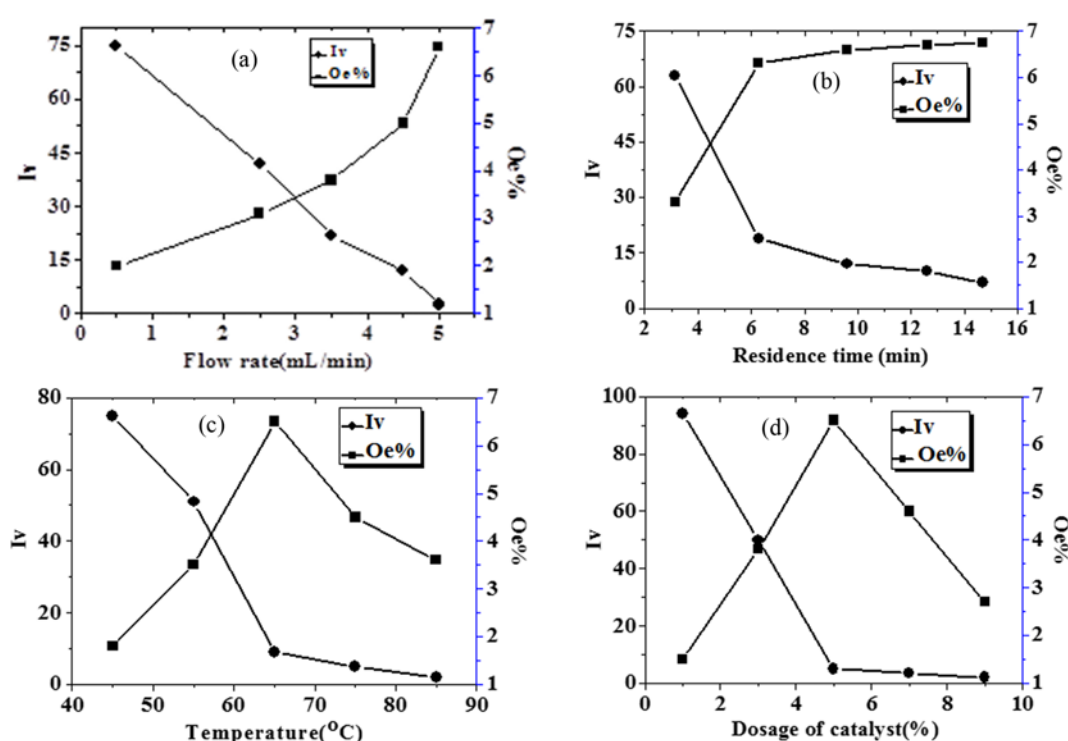

Fig. 3. Effect of (a) total flow rate, (b) residence time, (c) temperature, and (d) catalyst dosage on the mixing efficiency of epoxidation.

77.3 to 46.6. With further prolonging of reaction time, Oe first increases and then decreases. Similar results were already reported [6]. When the reaction time exceeds 12 h, the viscosity of the product mixture is significantly improved, Oe and Iv are close to zero. This is because a long reaction time can induce epoxy ring cleavage to form ethoxy/hydroxyl compounds [25]. Therefore, the batch process is not suitable for preparation of high-Oe EFAME.

Then the reaction conditions were optimized on TTGMR, including the flow rate, residence time, temperature, catalyst dosage, H_2O_2/-C=C- molar ratio, HAc/-C=C- molar ratio and stabilizer EDTA-2Na.

2. Effect of Flow Rate on the Mixing Efficiency of TTGMR

The effect of total flow rate (feed flow rate of FAME and peracetic acid) was investigated at H_2O_2/-C=C- ratio=1.2 : 1, HAc/-C=C- ratio=1.0 : 1, 1 wt% EDTA-2Na, catalyst dosage=5 wt% and

residence time=6.28 min at 65 °C. As shown in Fig. 3(a), as the total flow rate rises from 0.5 to 4.5 mL/min, the Oe increases from 2.9 to 4 and Iv decreases from 57.8 to 37.5. When the flow rate further rises to 5 mL/min, Oe increases to 6.6 and Iv decreases to 2.2. With the increase of flow rate, the fluid flow and inner wall shear stress promote the transfer of fluid mass and heat, leading to the significant changes of Iv and Oe. The total flow rate was set at 5 mL/min in the following experiments. As reported, with the increase of volume flow, the entropy would be accelerated by introducing energy to overcome the surface two-phase tension, so the reaction performance was enhanced with higher Oe and lower Iv [26].

3. Effect of Residence Time

The effect of residence time was investigated with the reaction conditions mentioned above. As shown in Fig. 3(b), the prolonged residence time results in the increase of Oe. The Oe of the epoxi-

dation increases rapidly at the residence time from 3.14 to 7.85 min (corresponding delay loop length=2 to 4 m), but from 7.85 to 14.7 min, Oe only slightly increases (delay loop length=4 to 10 m). Therefore, the appropriate residence time is 7.85 min with Oe of 6.6. In comparison, at least 6.5 h was needed to reach such Oe for the same biodiesel epoxidation carried out in the three-neck flask [6], indicating the epoxidation in a microreactor is considerably fast.

4. Effect of Reaction Temperature

The effect of reaction temperature on Iv and Oe of FAME epoxidation is shown in Fig. 3(c). Oe is maximized to 6.5 (Iv=2.5) as the temperature rises from 40 to 65 °C. Both the epoxidation rate and epoxide ring cleavage rate increase with the temperature rise. Oe is maximized first and then decreases, but Iv continues to decline. When the temperature rises to 80 °C, the product viscosity is intensified and Oe is significantly lowered. The temperature rise accelerates the production of peracetic acid [27,28], which is the control step of epoxidation. The relatively high temperature can also cause the decomposition of H_2O_2, peracetic acid and epoxy products, which is unfavorable for improvement of Oe. Thus, the optimal temperature should be 65 °C.

5. Effect of Catalyst Dosage (Concentrated Sulfuric Acid)

Fig. 3(d) shows the effects of catalyst dosage on Iv and Oe of epoxidation. In TTGMR, when the catalyst dosage varies from 3 to 5 wt%, the Oe rapidly rises from 3.4 to 6.5. However, further increase of catalyst dosage leads to the fast decrease of Oe. The Iv is always reduced with the increase of catalyst dosage. These results indicate an appropriately small catalyst dosage can accelerate the peracetic-acid synthesis and the epoxidation, but a large dosage can cause the opening of the ethylene oxide epoxy, thus resulting in the decrease of Oe [29].

6. Effect of HAc/-C=C- Ratio

The effect of the HAc/-C=C- ratio from 0.6 : 1 to 1.4 : 1 was investigated in the TTGMR. Results show Oe grows from 2.3 to 6.5 with the HAc/-C=C- ratio rising from 0.6 : 1 to 1 : 1, but decreases with the HAc/-C=C- ratio increasing from 1 : 1 to 1.4 : 1. High HAc amount would accelerate the epoxidation and ring-opening, accompanied with the side reaction of epoxy compounds and water. All of these reactions make the Oe decrease and darken the final product [30]. Thus, the optimal HAc/-C=C- ratio is 1 : 1.

7. Effect of H_2O_2/-C=C- Ratio

The effect of H_2O_2/-C=C- ratio on the Iv and Oe of epoxidation was investigated in TTGMR. Results show the Oe reaches 6.5 when the H_2O_2/-C=C- ratio increases from 1.0 : 1 to 1.2 : 1. With further increase of the H_2O_2/-C=C- ratio, both Oe and Iv begin to decline. At the beginning, the increased usage of H_2O_2 can make up the partial decomposition, and thus is favorable for the formation of peracetic acid and EFAME. However, the presence of water and excessive H_2O_2 easily induces ring opening to form double-hydroxyl compounds, resulting in the decrease of Oe [31].

DISCUSSION

The above results indicate TTGMR outperforms both HPIMM and HD. The entrance channel of the T-micromixer is 50 μm wide, where the channel of T-type mixing point is 100 μm wide. The flow patterns will not change in such T mixer (Fig. 4).

On the other hand, the material of the microreactor slightly affects the epoxidation of FAME [26]. For example, the slit HPIMM structure could accelerate the mixing of oil-water phases, but its material, 316 L stainless steel, would promote the decomposition of H_2O_2 and peracetic acid, resulting in lower Oe. As for TTGMR, the reagents are pumped into the straight channel that has turning points. Fig. 4(a) shows the formation of the alternating aqueous and organic segments in the segmented flow. The generated circulation can reduce the thickness and diffusion length of the droplet boundary layer, which accelerates mixing and diffusion by lessening the con-
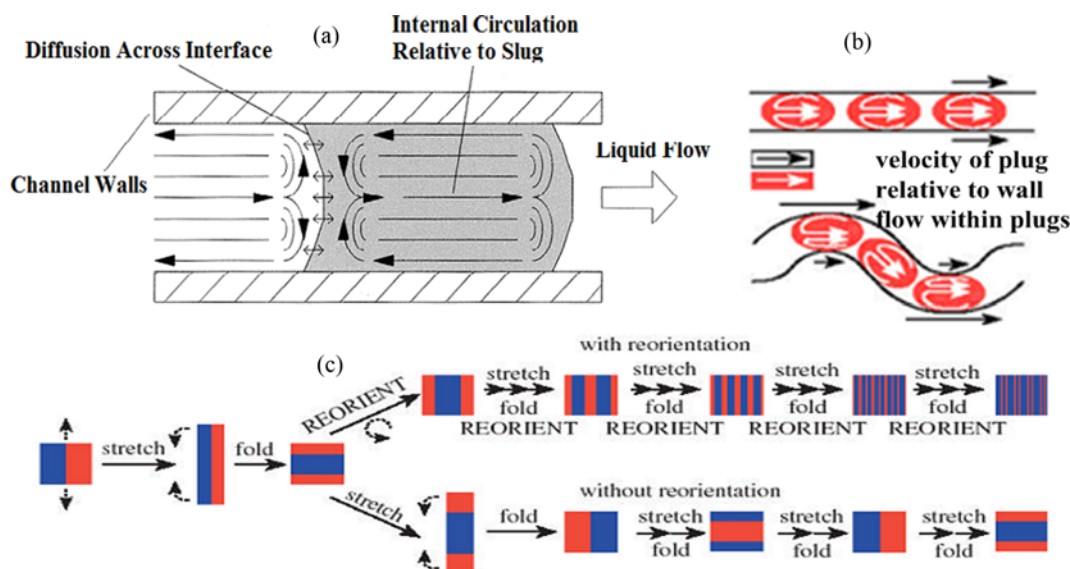

Fig. 4. Circulation patterns generated inside each liquid slug (a); Flows in plugs through a straight channel and a winding channel (b) [31]; mixing process based on the Baker's transformation principle (upper) or without reorientation (lower) does not decrease the striation thickness (c) [31].

Table 2. The oxidation stability test of EFAME

Items Samples	Acid value (mg KOH/g)	Iodine value (g/100 g)	Epoxy value (equivalent number/100 g)	Viscosity (mPa·s, 30 °C)
15 Days	0.38	2.50	6.50	21.10
30 Days	0.40	2.20	6.35	21.17

centration gradients [24,32,33]. In the tortuous microchannels of the T-mixer, the recirculation, stretching and folding of the solution enhance the mixing (Fig. 4(b), 4(c)) [32,34-36].

Compositions of biodiesel FAME with vegetable oil are not similar to double bond with react site for epoxidation; results of epoxidation of various biodiesel FAME and un-reacted FAME after reaction are listed as follows. For example, a highly efficient and green strategy for the epoxidation of methyl oleate (yields of epoxide 87-93%), has been explored [7]. The maximum conversion of unsaturated carbon bonds of used-oil biodiesel (95.8%) was obtained with the maximum epoxy compound selectivity (100%) [37]. The epoxidation of rapeseed oil methyl ester, the reaction products, which are of a similar distribution (mono-, di, and triepoxides vs. mono-, di-, and triunsaturates) as the substrate, and an overall conversion related to C=C-bonds of 95%?selectivity 88-92% were achieved [38].

Viscosity is one important physic-chemical property. FAME and EFAME have dynamic viscosity of 8 and 21.09 mPa·s at 30 °C, respectively, measured by an NDJ-99 rotary viscometer (Chengdu Instrument Factory, China). Thus, the epoxidized FAME has higher viscosity than bare FAME at the same temperature, because C=C is converted to epoxy groups after epoxidation, which increases the amount of oxygen atoms and greatly improves the molecular polarity. Therefore, the molecular chains form hydrogen bonds, promoting intermolecular interaction, and ultimately improve the viscosity and viscous flow activation energy. At the same time, some -OH groups formed from epoxy groups would shrink and cross-link together to form glue-like by-products [32].

The oxidation stability test is a very important characteristic for the epoxidation product. We found that the product is relatively stable by acid value, iodine value and epoxy value and the viscosity test to the samples which were stored for 15 days and 30 days, respectively. The results are listed in Table 2. In our future work, the oxidation stability and average molecular weight control will be conducted according to international test method.

CONCLUSIONS

TTGMR was chosen and used in continuous synthesis of EFAME starting from FAME and peracetic acid. The optimized reaction conditions are as follows: temperature=65 °C, flow rate=5 mL/min, residence time=6.28 min, catalyst dosage=5 wt%, 40 wt% H_2O_2, H_2O_2/-C=C- molar ratio=1.2 : 1, HAc/-C=C- molar ratio=1.0 : 1 and 1 wt% EDTA-2Na (stabilizer). At such reaction conditions, EFAME with the maximum Oe 6.5 was obtained.

ACKNOWLEDGEMENTS

NOMENCLATURE

Iv	:	iodine value [g /100 g]
Oe	:	epoxy value [equivalent number/100 g]
X	:	acid value [mg KOH/g]
i.d.	:	inner diameter of the delay loop [mm]

SUPPORTING INFORMATION

Additional information as noted in the text. This information is available via the Internet at http://www.springer.com/chemistry/journal/11814.

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Supporting Information

Efficient continuous epoxidation of biodiesel in a microstructured reactor

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ATTACHMENT

The acid value is defined as the amount of KOH (mg) required to neutralize 1 g of a sample (GB-T-1668-2008).

Principle: After the sample is dissolved in a solvent of ethanol, using phenolphthalein as indicator, titrated with sodium hydroxide standard solution.

Reagents:

Absolute alcohol

Sodium hydroxide standard solution C (NaOH)=0.05 mol/L, C (NaOH)=0.1 mol/L.

Potassium hydroxide standard solution C (KOH)=0.05 mol/L, C (KOH)=0.1 mol/L.

Phenolphthalein indicator 10 g/L, The phenolphthalein tune into a light pink with dilute alkali lye

Apparatus:

Conical flask 100-125 mL, or 250 mL

Microburet scale division is not greater than 0.02 mL

Procedure

After 50 g samples was dissolved in 50 ml ethanol solvent in a conical flask, then titrated with 0.1 mol/L KOH solution, using phenolphthalein as indicator, until the end-point indicated by the light pink color continuous appears at least 5 s after vigorous shaking.

Calculation

$$X = \frac{(V - V_0) \times c \times M}{m}$$

In the above formula, X is acid value of the sample, the unit for X is mg/g;

V is the volume, in milliliters, of sodium hydroxide solution used for the determination;

V_0 is the volume, in milliliters, of sodium hydroxide solution used for the blank test;

C is the concentration, in moles per liter, of the sodium hydroxide standard solution;

m is the mass, in grams, of the test portion;

M is the molar mass of sodium hydroxide solution, in g/mol.

Iodine value (I_V) is defined as the mass of iodine (g) consumed by 100 g of a sample (GB/T 5532-2008). Iv is often used to determine the amount of unsaturation in fatty acids.

Principle: After the sample is dissolved in a solvent, adding the Wijs reagent reacted for a certain time, adding potassium iodide and water, titrated with sodium thiosulfate solution, precipitated iodine.

Reagents:

Potassium iodide solution, mass contention (100 g/l), not containing iodate or free iodine.

Sodium thiosulfate solution, standard volumetric solution amount of substance concentration c(Na$_2$S$_2$O$_3$·5H$_2$O)=0.1 mol/l, standardized not more than 7 days before use.

Starch solution, mix 5 g of soluble starch in 30 ml of water and add to 1,000 ml of boiling water. Boil for 3 min and allow to cool. Prepare fresh starch solution every day.

Solvent, prepared by mixing one volume of cyclohexane (50 ml) and one volume of glacial acetic acid (50 ml).

Wijs reagent, containing iodine monochloride in acetic acid. The I/Cl ratio of the Wijs reagent shall be within the limits 1, 10±0.1. Wijs reagent is sensitive to temperature, moisture, and light. Store in the dark at <30 °C.

Apparatus

Glass weighing scoops

Conical flasks, capacity 500 ml, fitted with ground glass stoppers and showing no evidence of the presence of moisture.

Analytical balance, readability 0.0001 g and weighing accuracy 0.001 g.

Volumetric flask, capacity 1,000 ml.

Pipette, capacity 25 ml, fitted with an aspiration bulb.

Burette, capacity 25 ml and 50 ml, graduated in 0.1 ml divisions, auto titrator, as an alternative.

Procedure

Place the glass scoop containing the test portion in a 500 ml conical flask and add the solvent. Add 25 ml of Wijs reagent by pipette. Insert the stopper, swirl the contents and place the flask in the dark. Melt and dissolve fats and oils in warm solvent. Prepare a blank with solvent and reagent, but omitting the test portion. For samples having an Iv below 150, leave the flask in the dark for 1 h. At the end of the reaction time, add 20 ml of potassium iodide and 150 ml of water.

Titrate against standard sodium thiosulfate solution until the yellow colour due to iodine has almost disappeared. Add a few drops of the starch solution and continue the titration until the blue colour just disappears after vigorous shaking. Record the volume V_2, of sodium thiosulfate solution required to reach the endpoint. Note that potentiometric determination of endpoint is permissible.

Calculation

$$Iv = \frac{12.69 \times c \times (v_1 - v_2)}{m}$$

In the above formula, Iv is iodine value of the sample, in grams per100 g sample;

V_1 is the volume, in milliliters, of sodium thiosulfate solution used for the blank test;

V_2 is the volume, in milliliters, of sodium thiosulfate solution used for the determination;

C is the concentration, in moles per liter, of the sodium thiosulfate solution;

m is the mass, in grams, of the test portion;

M is the molar mass if NaOH, in g/mol.

Epoxy value (Oe) is defined as the oxygen content in 100 g of a sample (GB/T 1677-2008). Oe underlies the determination of product quality and reflects the epoxidation degree of double bond in the molecular structure.

Reagents:

Hydrochloric acid [7647-01-0];

Acetone [67-64-1];

95% ethanol [64-17-5];

Hydrochloric acid- Acetone solution: Mixing hydrochloric acid and acetone solution in volume ratio of 1 : 40, stored in a sealed glass bottle, prepared when it will be used;

Sodium hydroxide standard solution C (NaOH)=0.15 mol/L, C (NaOH)=0.01 mol/L;

Phenolphthalein indicator Take 1 grams of phenolphthalein dissolved in 100 ml 95% ethanol;

Cresol red;

Thymol blue;

Mixed indicator

0.1% Cresol Red Dissolve 0.1 g Cresol Red in 26 ml of 0.1 M sodium hydroxide, after it is dissolved, the solution was diluted with distilled water to the 100 mL mark;

0.1% Thymol blue Dissolve 0.1 g thymol blue in 22 ml of 0.01 M sodium hydroxide, after it is dissolved, the solution was diluted with distilled water to the 100 mL mark;

Take 10 mL 0.1% Cresol Red solution mixed well with 30 mL 0.1% thymol blue, the mixer was neutralized with 0.01 M NaOH solution and 0.01 M HCl solution (Mixed indicator changes color when PH=9.8).

Apparatus

Grinding mouth Erlenmeyer Conical flask with stopper flasks, capacity 250 ml;

Volumetric flask, capacity 1,000 ml;

Basic Buret 50 ml, graduated in 0.01 ml divisions;

Straight condenser, Length 40 cm;

Pipette, capacity 25 ml, fitted with an aspiration bulb;

Oil bath;

Procedure

Place the 0.5 g-1.0 g sample in a 250 ml conical flask a, add 20 ml of hydrochloric acid-acetone reagent by pipette, insert the stopper, swirl the contents and place the flask in the dark, allowed to stand for 30 minutes. And add 5 drops of mixed indicator, titrated with 0.15 M sodium hydroxide standard solution, till color changes to violet blue, the blank test was accomplished.

Calculation

$$Oe = \frac{\left[V - \left(V_1 - \dfrac{V_2}{G} \times W\right)\right] N \times 0.016}{W} \times 100$$

In the above formula, O_e is epoxy value of the sample, epoxy values are expressed as a percentage;

V is the volume, in milliliters, of sodium hydroxide solution used for the blank test;

V_1 is the volume, in milliliters, of sodium hydroxide solution used for the determination;

V_2 is the volume, in milliliters, of sodium hydroxide solution used for the determination of acid value;

N is the concentration, in moles per liter, of the sodium hydroxide solution;

W is the mass, in grams, of the test portion;

G is the mass, in grams, of the test portion for determination of acid value;

0.016 is the molar mass, in gram per mol.

Table 1 composition of FAME raws.