



Contents lists available at ScienceDirect

Bioresource Technology

journal homepage: www.elsevier.com/locate/biortech

Production of biodiesel and lactic acid from rapeseed oil using sodium silicate as catalyst

Yun-Duo Long^{a,b}, Feng Guo^a, Zhen Fang^{a,*}, Xiao-Fei Tian^a, Li-Qun Jiang^a, Fan Zhang^a

^a Biomass Group, Laboratory of Tropical Plant Resource Science, Xishuangbanna Tropical Botanical Garden, Chinese Academy of Sciences, 88 Xuefu Road, Kunming, Yunnan Province 650223, China

^b School of Life Science, University of Science and Technology of China, 443 Huangshan Road, Hefei, Anhui Province 230027, China

ARTICLE INFO

Article history:

Received 6 January 2011

Received in revised form 3 April 2011

Accepted 4 April 2011

Available online xxxx

Keywords:

Biodiesel

Glycerol

Hydrothermal

Lactic acid

Sodium silicate

ABSTRACT

Biodiesel and lactic acid from rapeseed oil was produced using sodium silicate as catalyst. The transesterification in the presence of the catalyst proceeded with a maximum yield of 99.6% under optimized conditions [3% (w/w) sodium silicate, methanol/oil molar ratio 9/1, reaction time 60 min, reaction temperature 60 °C, and stirring rate 250 rpm]. After six consecutive transesterification reactions, the catalyst was collected and used for catalysis of the conversion of glycerol to lactic acid. A maximum yield of 80.5% was achieved when the reaction was carried out at a temperature of 300 °C for 90 min. Thus, sodium silicate is an effective catalyst for transesterification and lactic acid production from the biodiesel by-product, glycerol.

© 2011 Elsevier Ltd. All rights reserved.

1. Introduction

The production of biodiesel from feed stock such as soybean and rapeseed oil, is generally accomplished by transesterification in the presence of either acids or bases, such as sulfuric acid or sodium hydroxide (Deng et al., 2010). The catalytic efficiency of base catalysts is higher than that of acid catalysts; however, due to the fact that crude oils and fats contain small amounts of free fatty acids (FFAs) or water, use of homogeneous basic catalysts will result in the formation of soap and a decrease in biodiesel yield (Ma and Hanna, 1999; Kawashima et al., 2008). Moreover, removal of these homogeneous catalysts after reactions is difficult.

Compared with homogeneous basic catalysts, heterogeneous catalysts can avoid saponification of FFAs, and are easily separated from product mixtures. Examples include Mg–Al hydrotalcites (Deng et al., 2011), $K_2CO_3/\gamma-Al_2O_3$ (Liu et al., 2010), TiO_2-MgO (Wen et al., 2010), Zr–La oxides (Sun et al., 2010). Although some of these catalysts can achieve good to excellent biodiesel yields, they may function only at high temperatures, require long reaction times, be moisture sensitive and high in cost.

Sodium silicate is also an effective heterogeneous base catalyst in biodiesel production from soybean oil (Guo et al., 2010; Xiu and Guo, 2010). Since it is known that glycerol, a by-product of biodie-

sel production, can be converted to lactic acid under alkaline hydrothermal conditions (Kishida et al., 2005; Shen et al., 2009; Ramírez-López et al., 2010), this study was undertaken to determine if sodium silicate could also be used to catalyze this conversion. Therefore, sodium silicate was used for transesterification of rapeseed oil, recovered from the reaction mixture and directly used for glycerol conversion to lactic acid.

2. Methods

2.1. Materials

Sodium silicate (19.3–22.8 wt.% of Na_2O), dehydrated methanol, sodium hydroxide (96%), potassium hydroxide (85%), LA (85.5–90%), formic acid (88%), acetic acid (99.5%), and acrylic acid (98%) were purchased from Xilong Chemical Corp., Shantou, China. Refined rapeseed oil was obtained from a supermarket. Glycerol (99.9%) was obtained from Sigma–Aldrich (Shanghai, China). Crude glycerol (89% purity, methanol 1%, water and other components including soaps and lipids 10%) was from the biodiesel production. Deionized water was used in all experiments.

2.2. Biodiesel production

Sodium silicate was firstly dehydrated at 200 °C for 20 min, then calcined at 400 °C for 2 h, and finally triturated and passed through a 200 mesh sieve as catalyst for biodiesel production.

* Corresponding author. Tel.: +86 871 5163360; fax: +86 871 5160916.

E-mail addresses: zhenfang@xtbg.ac.cn, zhen.fang@mail.mcgill.ca (Z. Fang).

URL: <http://brg.groups.xtbg.ac.cn/> (Z. Fang).

The transesterification of rapeseed oil to biodiesel was carried out in a 250 mL three-necked round-bottom flask equipped with a mechanical stirrer and a water-cooled condenser. The flask was loaded with 30 g of rapeseed oil, heated to the desired temperature (e.g., 60 °C), and the desired amount of methanol and catalyst without preheating were added to start the transesterification with stirring for the desired reaction time. The heating time was considered negligible compared with reaction time (e.g., 60 min). After completion of the reaction, catalyst and excess methanol were recovered by centrifugation at 5000 rpm for 15 min and distillation, respectively.

2.3. Hydrothermal conversion of glycerol

Two mL of 0.3 M glycerol and sodium silicate (0.25–1.25 M) were placed in a 316-stainless steel (SS) seamless tubular reactor (12 mm outer diameter, 2 mm wall thickness, 100 mm length with two-end caps, inner reaction volume of 6 mL). The reactor was sealed, purged with nitrogen, and placed in an electric furnace preheated to the desired temperature. The reaction mixture was heated at 8 °C/min resulting in heating times of between 28 and 40 min to reach 260 °C and 320 °C. As the reaction proceeds very slowly below 250 °C, the heating time was not included in the reaction time. After the reaction was completed, the reactor was cooled in cold water.

2.4. Product analyses

Biodiesel was analyzed with a gas chromatography (GC-2014, Shimadzu, Japan) equipped with a capillary column Rtx-Wax (30 m × 0.25 mm × 0.25 μm) and a flame ionization detector. Samples (1 μL) were injected at an oven temperature of 220 °C. Helium was used as carrier gas. The temperatures of injector and detector were 260 °C and 280 °C, respectively. An internal standard (heptadecanoic acid methyl ester) was used for quantitative analyses.

Liquid samples (2 mL) from glycerol conversion were diluted with deionized water to 25 mL (dilution ratio of 12.5), and then their pH was adjusted to 2–3 with sulfuric acid. Before analysis, samples were filtered through 0.45 μm nylon syringe filters. Organic acids were analyzed with a high-pressure liquid chromatography (HPLC, LC-20A, Shimadzu, Japan), fitted with an HPX-87H column and a UV detector detected at 210 nm. The mobile phase was 5 mM H₂SO₄ with a flow rate of 0.6 mL/min, and the column temperature was 50 °C. Glycerol was analyzed by HPLC under the same conditions using a refractive index (RI) detector. LA yield was defined as mole percentage of LA to the initial glycerol. Optical purity of L-(+)-LA was determined by a SBA-40D biosensor (Biology Institute of Shandong Academy of Sciences, China). The L-(+)-LA purity was defined as mole percentage of L-(+)-LA to the total LA (including L-(+)-LA and D-(-)-LA). Glycerol conversion rate was calculated as mole percentage of the converted glycerol to the initial glycerol.

3. Results and discussion

3.1. Biodiesel production

The optimum transesterification conditions were determined to be 3% (w/w) catalyst, a 9:1 ratio of methanol and oil, a reaction time of 60 min, a reaction temperature of 60 °C and a stirring rate of 250 rpm. These conditions are similar to those reported previously (Guo et al., 2010; Xiu and Guo, 2010). A yield of 99.6% was achieved when the catalyst was used for the first time. The yield decreased to 92% after the catalyst was reused six times (Fig. 1). Only approximately 0.2% of the catalyst was lost totally after six

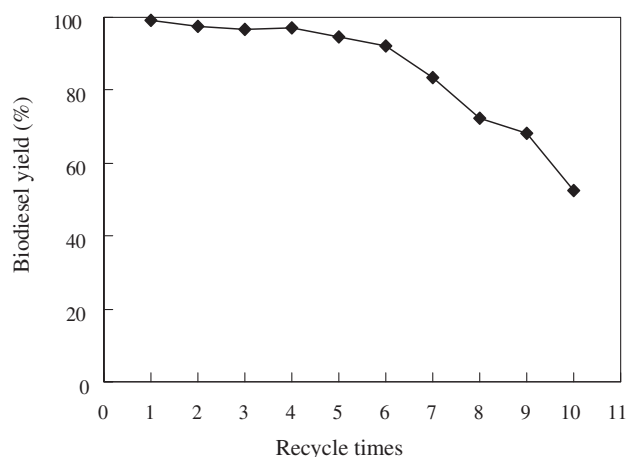


Fig. 1. Biodiesel yields under optimal conditions (methanol/oil molar ratio 9/1, reaction time 60 min, reaction temperature 60 °C and stirring rate 250 rpm) in the presence of 3% (w/w) of fresh and recycled sodium silicate catalyst.

cycles, and it is therefore unlikely that this quantitative loss was responsible for the decreased biodiesel yield. More likely, qualitative changes such as the absorption of water by the catalyst and subsequent breakage of Si–O–Si bonds and loss of alkaline groups as observed by Guo et al. (2010) were responsible.

3.2. Hydrothermal production of lactic acid

3.2.1. High-purified glycerol (99.9%) as raw material

Lactic acid yields and glycerol conversion rates in response to reaction temperature and time are presented in Fig. 2a and b. It should be noted that all the experimental values in Fig. 2 are from single experiments without repetition except the maximum values obtained under the conditions: reaction temperature 300 °C, reaction time 90 min, glycerol concentration 0.3 M, catalyst concentration 0.25–1.25 M. These maximum values are averaged from triplicate experiments with standard errors (σ) below 0.5%. LA yield and glycerol conversion were less than 40% at 260 °C, but nearly 100% when the reaction was carried out at 300 °C for 90 min. The optimum temperature of 300 °C is the same as that reported by Kishida et al. (2005) and Shen et al. (2009) but 20 °C higher than that reported by Ramírez-López et al. (2010) who used NaOH as catalyst. The decrease in LA yield above 300 °C could be due to thermal degradation of LA (Mok et al., 1989; Lira and McCrackin, 1993; Aida et al., 2009).

The lactic acid yields in the presence of different amounts of catalyst are shown in Fig. 2c. The data indicate that a concentration of 0.625 M was sufficient for maximum lactic acid yields. The lactic acid yield was 90.7% when fresh catalyst was used and dropped to 80.5% when catalyst that had been used for six transesterification cycles was employed (Table 1). In each case, lactic acid was the predominant product, but some formic acid, acetic acid and acrylic acid was also detected by HPLC (Table 1). A small decrease in the L-(+)-LA yield was observed with the reused catalyst (Table 1).

3.2.2. Crude glycerol from biodiesel production as raw material

Based on the above results, three repeated tests for crude glycerol were conducted at reaction temperature 300 °C for 90 min. An LA yield of 89 ± 0.3% was achieved when 3 M crude glycerol and 1.5 M catalyst concentration (a molar ratio of glycerol to catalyst of 2) was used. This yield is only slightly lower than that obtained with pure glycerol. This result indicates that crude glycerol from biodiesel production can be used to produce LA as effective as pure glycerol.

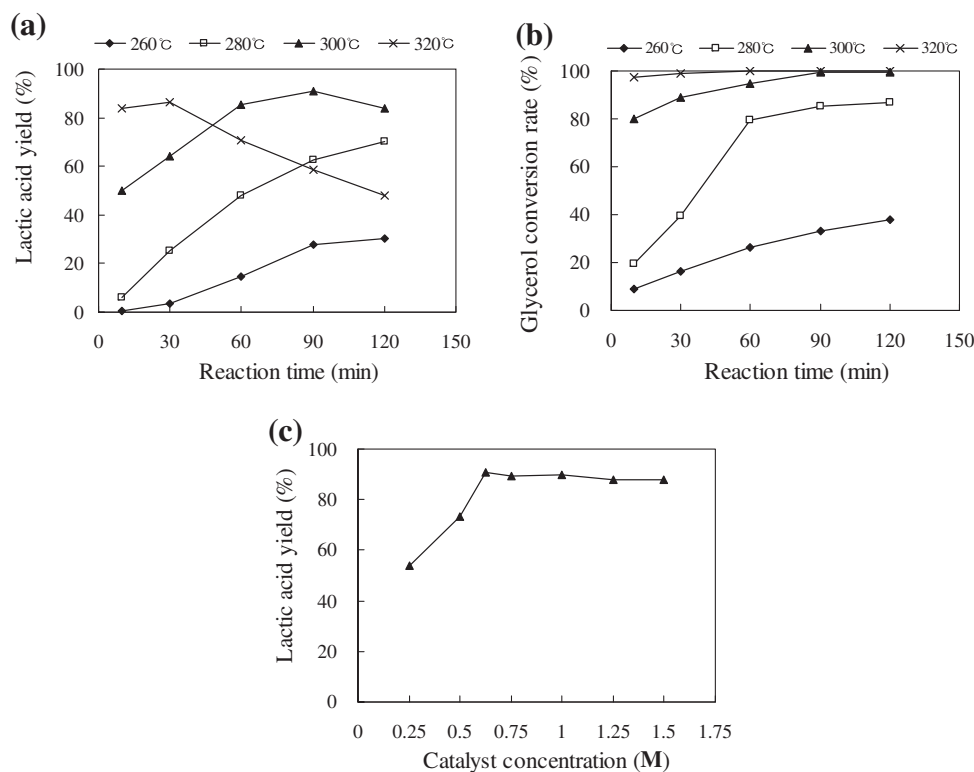


Fig. 2. Lactic acid yields and glycerol conversion rates in response to reaction temperature, reaction time and lactic acid yields in response to concentration of sodium silicate. Experimental conditions: (a) and (b) glycerol concentration 0.3 M, catalyst concentration 0.625 M; (c) at 300 °C, glycerol concentration 0.3 M and reaction time 90 min.

Table 1

Yields of products from hydrothermal conversion of glycerol with sodium silicate:

	Na ₂ SiO ₃ ^a	Na ₂ SiO ₃ ^b
Lactic acid (%)	90.7	80.5
Formic acid (%)	0.3	0.2
Acetic acid (%)	1.2	1.0
Acrylic acid (%)	0.1	0.15
Glycerol conversion rate (%)	99.6	92.8
L-(+)-Lactic acid (%)	42.8	41.0

Experimental conditions: 300 °C, 90 min reaction time, and 0.625 M catalyst concentration.

^a Fresh sodium silicate.

^b Used calcined sodium silicate after transesterification of rapeseed oil for six recycling times.

4. Conclusions

The current study has demonstrated that sodium silicate can be used as a catalyst for transesterification of rapeseed oil and subsequently without modification for the production of lactic acid from glycerol. The sodium silicate catalyzed reaction carried out at 300 °C yielded 80.5% lactic acid and only minor amounts of formic, acetic acid and acrylic acid. The L-(+)-lactic acid yield was about 40%. Lactic acid separation from aqueous effluents needs to be further investigated before the process could be industrially implemented.

Acknowledgements

The authors wish to acknowledge the financial support from Chinese Academy of Sciences [Bairenjihua and Knowledge innovation key project (KSCX2-YW-G-075)], and China National Natural Science Foundation (No: 21076220).

References

- Aida, T.M., Ikarashi, A., Saito, Y., Watanabe, M., Smith Jr., R.L., Arai, K., 2009. Dehydration of lactic acid to acrylic acid in high temperature water at high pressures. *J. Supercrit. Fluid* 50, 257–264.
- Deng, X., Fang, Z., Liu, Y.H., 2010. Ultrasonic transesterification of *Jatropha curcas* L. oil to biodiesel by a two-step process. *Energy Convers. Manage.* 51, 2802–2807.
- Deng, X., Fang, Z., Liu, Y.H., Yu, C.L., 2011. Production of biodiesel from *Jatropha* oil catalyzed by nanosized solid basic catalyst. *Energy* 36, 777–784.
- Guo, F., Peng, Z.G., Dai, J.Y., Xiu, Z.L., 2010. Calcined sodium silicate as solid base catalyst for biodiesel production. *Fuel Process. Technol.* 91, 322–328.
- Kawashima, A., Matsubara, K., Honda, K., 2008. Development of heterogeneous base catalysts for biodiesel production. *Bioresour. Technol.* 99, 3439–3443.
- Kishida, H., Jin, F.M., Zhou, Z.Y., Moriya, T., Enomoto, H., 2005. Conversion of glycerin into lactic acid by alkaline hydrothermal reaction. *Chem. Lett.* 34, 1560–1561.
- Lira, C.T., McCrackin, P.J., 1993. Conversion of lactic acid to acrylic acid in near-critical water. *Ind. Eng. Chem. Res.* 32, 2608–2613.
- Liu, X.H., Xiong, X.Y., Liu, C.M., Liu, D.Y., Wu, A.J., Hu, Q.L., Liu, C.L., 2010. Preparation of biodiesel by transesterification of rapeseed oil with methanol using solid base catalyst calcined K₂CO₃/γ-Al₂O₃. *J. Am. Oil Chem. Soc.* 87, 817–823.
- Ma, F.R., Hanna, M.A., 1999. Biodiesel production: a review. *Bioresour. Technol.* 70, 1–15.
- Mok, W.S., Antal Jr., M.J., Jones Jr., M., 1989. Formation of acrylic acid from lactic acid in supercritical water. *J. Org. Chem.* 54, 4596–4602.
- Ramírez-López, C.A., Ochoa-Gómez, J.R., Fernández-Santos, M., Gómez-Jiménez-Aberasturi, O., Alonso-Vicario, A., Torrecilla-Soria, J., 2010. Synthesis of lactic acid by alkaline hydrothermal conversion of glycerol at high glycerol concentration. *Ind. Eng. Chem. Res.* 49, 6270–6278.
- Shen, Z., Jin, F.M., Zhang, Y.L., Wu, B., Kishida, A., Tohji, K., Kishida, H., 2009. Effect of alkaline catalysts on hydrothermal conversion of glycerin into lactic acid. *Ind. Eng. Chem. Res.* 48, 8920–8925.
- Sun, H., Ding, Y.Q., Duan, J.Z., Zhang, Q.J., Wang, Z.Y., Lou, H., Zheng, X.M., 2010. Transesterification of sunflower oil to biodiesel on ZrO₂ supported La₂O₃ catalyst. *Bioresour. Technol.* 101, 953–958.
- Wen, Z.Z., Yu, X.H., Tu, S.T., Yan, J.Y., Dahlquist, E., 2010. Biodiesel production from waste cooking oil catalyzed by TiO₂-MgO mixed oxides. *Bioresour. Technol.* 101, 9570–9576.
- Xiu, Z.L., Guo, F., 2010. Application of novel solid acid and base catalysts in biodiesel synthesis. *J. Biotechnol.* 150, S178.