Journal of Cleaner Production xxx (2015) 1–10

Contents lists available at ScienceDirect

Journal of Cleaner Production

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

Improved thermo-oxidative stability of structurally modified waste cooking oil methyl esters for bio-lubricant application

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ARTICLE INFO

Article history:
Received 31 October 2014
Received in revised form
8 June 2015
Accepted 10 June 2015
Available online xxx

Keywords:
Waste cooking oil methyl esters
Bio-lubricant basestock
Analysis of variance
Catalyst reusability
Thermo-oxidative stability

ABSTRACT

This communication bridges the gap between conventional and alternative (renewable) lubricant basestocks in the lubricant industry. Waste cooking oil methyl esters (WCOME) originated from soybean oil was prepared by aiming at the maximum esters conversion. Esters conversion were confirmed and supported by thin layer chromatography and nuclear magnetic resonance spectral techniques (^{1}H, ^{13}C). WCOME bio-lubricant basestock was synthesized via *In-situ* epoxidation using acidic ion-exchange resin as a heterogeneous catalyst. A statistical experimental design, response surface methodology (RSM) was implemented to optimize the experimental conditions and to understand the interactions among the process variables. The optimum conditions inferred from the RSM were: temperature, 53.71 °C; catalyst loading, 28.17 wt%; time, 7.51 h; and H_2O_2, 1.72 mol. Products was confirmed and characterized by nuclear magnetic resonance spectroscopy (NMR), Fourier transform infrared spectroscopy (FTIR) and oxirane analysis by HBr titration method. At this optimum condition maximum epoxide content was found to be 5.8 mass%. Physico-chemical properties of WCOME and its epoxide were determined by standard methods and compared. Characterization results revealed that the structurally modified WCOME epoxide had improved viscosity and thermo-oxidative stability compared with unmodified WCOME. Overall, outcomes of the physico-chemical characterization data indicated that prepared epoxide can act as an alternative lubricant basestock for various industrial applications.

1. Introduction

Worldwide, consumption of renewable resources in industrial applications has become a topic of great interest in the federal, commercial and most importantly in consumer conscience (Tullao, 2007). By concerning eco-system over the use of fossil based products in various industries such as mining, farming and forestry have led to increased interest in the use of eco-friendly fluids (Metzger and Huttermann, 2009). In addition to that, arising environmental concerns are providing the impetus for increasing need and usage of vegetable oils as lubricant basestocks for various applications. Gawrilow (2004) reported that annually 10–15 million tons of fossil based oleo-chemicals enter the biosphere. However, during last eight years due to rapid industrialization and population growth, there is a high demand for higher-quality lube oils in the automobile industry. Conventionally, basestocks used for the formulation of lubricants is ecologically hostile mineral oil, which is derived from fossil resources. Currently, Indian lubricant industry is the seventh greatest lubricant market in the world and sixth largest automotive lubricant market, and its market is growing 7% annually. Since, lots of latest machinery, equipments, and vehicles coming on the roads every day, there is a huge scope for lubricant market (Anonymous, 2011). In 2011, an average raw material cost was raised 21% for manufacturers and according to an estimate, since 2005 annual utilization of lubricants is increasing along with prices (Anonymous, 2013). As per the approximation by Indian lubricant market, consumption will cross 2 MMT/a by 2014–15 (Anonymous, 2013). Various researchers and industrialists estimated that fossil based oils shortly might not be available. In this regard, vegetable/plant seed oils are perceived to be the most promising alternatives as they exhibit certain inherent technical

Acronyms: WCOME, waste cooking oil methyl esters; RSM, response surface methodology; WCO, waste cooking oil; OOC, oxirane oxygen content; ANOVA, analysis of variance; TLC, thin layer chromatography; NMR, nuclear magnetic resonance; RCCD, rotatable central composite design; PP, pour point; DSC, differential scanning calorimetry; TGA, thermogravimetric analysis; IV, iodine value; FFA, free fatty acid; KV, kinematic viscosity; FTIR, Fourier transform infrared spectroscopy.

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http://dx.doi.org/10.1016/j.jclepro.2015.06.046
0959-6526/

properties such as, ability for biodegradability and alike physico-chemical properties with conventional lubricant basestocks. Therefore, they may compete as an economical alternative with fossil based lubricant basestocks.

Compared to mineral oils, vegetable oils universally own higher flash point, eminent viscosity index, improved lubricity and lower evaporative loss. However, vegetable oils cannot be used directly as basestock oils for various applications due to their inadequate thermo-oxidative, hydrolytic stability, higher temperature sensitivity of tribological behaviour and miserable cold flow properties. In order to use plant seed oils as lubricant basestocks their structure need to be modified. In the present scenario, researchers much attention has been paid towards renewable resources (vegetable oils) to improve their physico-chemical and performance properties, so that they can compete with petro-based lubricants as an economical alternative. All the negative effects of plant oils are due to their inherent fatty acid composition, i.e. mainly due to presence of unsaturated fatty acids. Unsaturation limits the use of plant oil as an effective bio-lubricant basestock (Erhan and Asadauskas, 2000). So, there is a need to modify the structure of vegetable oils in order to make use of them effectively. Most of these problems can be resolved by modifying polyunsaturated sites in triacylglycerol structure of plant oils. Several advanced technological routes have been adopted to solve the problems related with plant oils in lubricant applications. Following are the possible alternatives to enhance the performance properties of vegetable oils as bio lubricants such as; genetic modification (Smith et al., 2007), additive treatment (Sharma et al., 2008), selective hydrogenation of unsaturated sites (Cermak et al., 2006), transesterification (Bokade and Yadav, 2007; Kleinaite et al., 2014) and chemical modification (Sharma et al., 2008; Li and Wang, 2015) i.e. structural modification by epoxidation reaction. Among them, most widely used technique is epoxidation, because it has opened up a wider range of feasible reactions, which can be carried out under moderate reaction conditions, due to the high reactivity of the oxirane ring. This three-member oxirane ring provides a more energetically favourable site for reaction and represents a chemical intermediate for the preparation of derivatives that would be difficult to obtain directly from the unsaturated bond (Borugadda and Goud, 2012). Structural modification of vegetable oils also enhances the thermo-oxidative stability and improved physico-chemical properties over unmodified vegetable oils and its esters.

However, in most of the cases edible oils and their esters (Sharma et al., 2008; Borugadda and Goud, 2012; Kleinaite et al., 2014) are used for epoxide synthesis. However, very scanty information is available on the use of edible waste oils/waste cooking oil methyl esters for epoxide synthesis. In this respect, waste cooking oil (WCO) or used frying oil methyl esters was prepared and used as an inexhaustible raw material for synthesis of bio lubricant basestock. All over the world, disposal of WCO and fats becomes a terrible environmental problem. This eco problem can be cleared by proper utilization and management of WCO by converting them into esters and using as a raw material for bio-lubricant basestock preparation. Utilization of WCO for synthesis of lubricant basestock significantly reduces the overall cost of final product. In India, 1.135 MMT/a waste fats and oils are generated (Mazumdar et al., 2012). Hence, current study investigates the epoxidation of methyl esters prepared from WCO using ion exchange resin (IR-120) as a heterogeneous acid catalyst. This communication also aims at studying the impact of various reaction parameters such as temperature, catalyst loading, hydrogen peroxide to oil molar ratio (substrate ratio) and reaction time on epoxidation reaction to attain maximum oxirane oxygen content (OOC). Response surface methodology was opted as an optimization tool to achieve an optimum reaction conditions.

2. Methodology

Following section elaborates the synthesis process of WCOME, detailed description of confirmation of methyl esters product using chromatography technique. Likewise, epoxidation reaction procedure, experimental design and statistical analysis are also explained in detail.

2.1. Alkali-catalysed transesterification of WCO and quality control of methyl esters by Thin Layer Chromatography (TLC)

Synthesis of high-quality methyl esters is also one of the major objectives in this communication. WCOME was prepared according the reported procedures (Borugadda and Goud, 2014; Farooq et al., 2013). Product was confirmed by nuclear magnetic resonance (NMR) spectral technique, in order to estimate the quality of biodiesel TLC technique was employed, which is a very commonly used technique to determine the number of compounds present in the reaction mixture. This technique provides qualitative and little information about the quantity of required product in a mixture of compounds. In our study, proper separation of methyl esters constituents was achieved using the solvent ratio of 90:10:1 (petroleum ether, diethyl ether and acetic acid) on a volume basis. Transesterification was conducted by varying the process variables at different ratios to maximize esters in the product (Table 1). Optimization experiments were attempted by altering the various reaction variables discussed elsewhere (Borugadda and Goud, 2014a). The best reaction conditions are drawn from the TLC analysis to prepare the WCOME in a bulk. From Fig. 1, it can be seen that apart from Run No-1 experiments conducted at all other conditions showed soap formation during water washing step, which lowers the methyl esters yield. Similarly, Ekman et al. (2013) and Fedosov et al. (2011) reported the quality and quantity analysis of biodiesel by TLC technique and findings of this study agrees well with the reported literature. Therefore, same reaction condition (Table 1, Run No-1) was adopted for methyl ester synthesis which yields 95% conversion. Physico-chemical properties of prepared methyl esters at optimum condition were determined using standard ASTM and AOCS official methods and were found to be within acceptable range of standards specifications.

2.2. Epoxidation reaction procedure, experimental design and statistical analysis

Response surface methodology (RSM) was used to explore the effect of various reaction variables on conversion of unsaturation into oxirane oxygen. Ranges of the process variables involved in this study are shown in Table 2, and experimental design matrix was created based on the process variable's range obtained from preliminary studies and reported in Table S1 of the supplementary data.

Table 1
Transesterification reaction conditions for optimum conversion of WCO into its methyl esters.

Run no	Oil to methanol molar ratio	Temperature (°C)	Catalyst loading (wt%)
1	1:6	60	1
2	1:6	55	1
3	1:6	65	1
4	1:9	60	1
5	1:9	55	0.5
6	1:9	60	0.5

Please cite this article in press as: Borugadda, V.B., Goud, V.V., Improved thermo-oxidative stability of structurally modified waste cooking oil methyl esters for bio-lubricant application, Journal of Cleaner Production (2015), http://dx.doi.org/10.1016/j.jclepro.2015.06.046