International Journal of ChemTech Research
CODEN(USA): IJCRGG ISSN : 0974-4290
Vol.6, No.1, pp 481-486, Jan-March 2014

Microwave-assisted Polymerization of Waste Cooking oil (WCO) with Maleic anhydride

Saeesh R. Chandelkar, V.Y.Karadbhajne*

Department of Oil Technology, Laxminarayan Institute of Technology, Rashtrasant Tukadoji Maharaj Nagpur University, Nagpur-440033, India.

***Corres.author: chandelkarsaeesh@gmail.com**

Abstract: The aim of the study is to synthesize malenized waste cooking oil and applying different microwave energies, temperature and time intervals and investigate the effects of these parameters on the percent conversion of the polymers. Waste cooking oil (WCO) has highly variable and uncontrolled quality. Along with flavor development, the oil undergoes chemical reactions such as Hydrolysis, Auto-oxidation, Oxidative Polymerization and Thermal Polymerization. All of the above chemical reactions alter the chemical structure of the oil molecules. Whilst keeping excellent control over molecular weights and molecular weight distributions. The present work is aimed at studying the microwave synthesis of polymers based on Vegetable oil and maleic anhydride. Various reaction temperatures, microwave power and time of reaction were studied. The idea is to develop a polymer with higher acid value and with good surfactant characteristics. It is also plan to compare the results of microwave synthesis with conventional synthesis in terms of quality as well as the physico-chemical characteristics of the products. The overall concept is to promote green chemistry by using waste cooking oil for making environment free from pollution to some extent. This article is aiming at utilization of this waste cooking oil for synthesis of malenized oil based oleo-chemicals.
Keywords: waste cooking oil (WCO), malenization of WCO, microwave heating, auto-oxidation, oxidative and thermal polymerization.

Introduction

The cooking oil is subjected to high temperatures during frying for relatively long periods of time, which causes oxidation of fatty acids and their subsequent transformations may cause unpleasant flavors and odors. Many researchers have pointed out that the thermally deteriorated oil leads to toxicity and can pose food hygiene problems. They have also pointed out that such oil exerts harmful influences upon the nutritive quality and the digestibility of the fried foods. Waste frying oil from household, restaurants and industrial application are regularly poured down the drains. Lack of information makes the consumer directly discard this used oil to sinks, toilet or even in rivers and soil.

There are some end uses of this waste cooking oil such as production of soap, energy by anaerobic digestion, thermal cracking and more recently production of biodiesel because this highly oxidized fats may have carcinogenic properties.

In the present work, experimental conditions have been worked out for getting a novel polymer based mainly on waste cooking oil and maleic anhydride. Waste cooking oil is collected from local restaurants. Per day and per capital production of waste cooking oil is calculated. Fatty acid profile and acid value is calculated. The results indicate that oils and fats experience various degrees of increase in saturation during cooking/frying use, with the magnitude of these changes varying from sample to sample, i.e., a high degree of randomness of composition is found in used frying oil samples. Properties of the samples that were investigated were acid value and viscosity which consistently increased with use[1,6].

Modification of this waste cooking oil is done to provide many desirable properties to it. These properties are result of high molecular weight. A number of methods have been suggested for improving the properties of waste cooking oil. One of the methods is adding unsaturated compound to the unsaturated part of the oil molecule, thus increasing its complexity and heat reactivity. Maleic anhydride is used as unsaturated compound for modification and the modified oil is known as Maleic treated or malenized oil. Since the maleic is added near the unsaturation section of the fatty acid radical it retards oxidation slightly so that maleic treated oils do not show greatly increased air-drying properties. Maleic anhydride is a dibasic acid which reacts with both conjugated and isolated double bonds. The possible chemical reactions are addition reaction of Maleic anhydride[11]. Conjugated acid reacts with maleic anhydride by Diels Alder reaction. The other reaction is direct addition of maleic anhydride at active methylene group. All the reaction is expected to give a useful active material for detergents. The high acid value copolymers have been neutralized with KOH to get water soluble composition with high surfactant activity[3,4].

Microwave heating is a modern and widely used method for food preparation. Changes of fats and oils have been intensively studied as the temperature of fat and oils can substantially increase during the operation. The temperature of the fat phase increases twice as fast during the microwave heating. Microwave heating occurs somewhat differently from conventional heating. The reaction vessel must be substantially transparent to the passage of microwaves. Heating of the reaction mixture does not proceed from the surface of the vessel; the vessel wall is almost always at a lower temperature than the reaction mixture. For microwave heating to occur, there must be some component of the reaction mixture that absorbs the penetrating microwaves. Microwaves will penetrate the reaction mixture, and if they are absorbed, the energy will be converted into heat. Just as with conventional heating, mixing of the reaction mixture may occur through convection, or mechanical means (stirring) can be employed to homogeneously distribute the reactants and temperature throughout the reaction vessel.

Experimental Work

Raw materials and their properties[2]

Used soybean oil is collected from local restaurant. Analysis of this waste cooking oil shows high acid value and low moisture content. WCO mainly contains oleic acid in final products. Raw materials used for malenization are used soybean oil and maleic anhydride. The analysis of waste soybean oil and composition of malenized oil are shown below.

Table no. 1 Analysis for waste soybean oil

Sr. no.	property	value
1	Acid value	81.35
2	Moisture content	0.02%
3	Colour	Blackish green
4	consistency	Thick

Table no. 2 Composition of malenized waste soybean oil

Material	Weight (gm)	Weight %
Used soybean oil	110	86.36
Maleic anhydride	15	13.64

Malenization of waste soybean oil[5,6]

Normally 5 – 15% maleic anhydride is added chemically to various vegetable oils to give a modified product with a higher acid value of 70 – 138. But we know that due to frying the free fatty acid content of used oil is much higher than unused vegetable oil. Therefore the process carried out for malenization of waste soybean oil is as follows.

1. As shown in table no. 1, waste soybean oil contains 0.02 % moisture, it is first heated at 70-80^{0}C for 10 min to reduce moisture.
2. When the temperature of waste soybean oil reaches to 70-80^{0}C, maleic anhydride is slowly added to oil as per the composition shown in table no. 2.
3. Continuous stirring is required for better mixing.
4. Temperature is maintained at 70-80^{0}C throughout the mixing.
5. Stirring is continued till we get bright yellow colored thick homogeneous mixture. Acid value and other properties are checked.
6. This malenized waste soybean oil is then introduced to microwave heating.

Table no. 3 Analysis of malenized waste cooking oil

Sr. no.	Property	Value
1	Acid value	246.53
2	Colour	Bright yellow
3	Consistency	Viscous

Microwave heating of maleic treated waste soybean oil

The CEM Focused Microwave™ Synthesis System, Model Discover, is used for microwave heating in present study. It is designed to enhance the ability to perform chemical reactions under controlled conditions on a laboratory scale. Microwave energy is applied to the vessel contents (reactants, catalysts, salts, solvents and/or solid supports) to accelerate the chemical reaction. The microwave absorption properties of some liquid and solid materials, due to their polar and ionic characteristics, have the capability to significantly enhance chemical reactions relative to traditional energy application (heating) techniques. Microwave heating is carried out in open vessel.

. In microwave heating, the temperatures are low enough to eliminate thermal degradation. Microwave can transfer energy directly to the reactive species, so-called “molecular heating”.

Figure no. 1 : The CEM Focused Microwave™ Synthesis System, Model Discover

Discover System - Front View

The steps involving in microwave heating of maleic treated waste cooking oil are given below[7,8].

1. About 20-25 gm of maleic treated waste cooking oil is taken in 100 ml conical flask.
2. Then it is introduced to the microwave reactor and then temperature, microwave power and time are adjusted as shown in table no. 4.
3. The mixture is heated for various temperature, power and time period in microwave reactor by setting the time and temperature of reactor.
4. After certain time period, reactor is stopped automatically. After cooling, reaction mixture is taken out of the reactor.
5. Acid value of this microwave heated malenized oil is calculated. Data is presented in Table no. 4.

Table no. 4 Microwave synthesis of maleic treated waste soybean oil

Sr. no.	Temperature (^{0}C)	Microwave power (watt)	Time (min)	Acid value
1	100	75	5	86.07
2	100	100	5	75.45
3	**125**	**100**	**4**	**65.84**
4	125	125	5	74.33
5	160	150	3	79.38
6	180	160	3	78.54
7	140	130	5	67.04
8	**160**	**160**	**5**	**65.076**
9	200	180	2.40	77.14
10	**200**	**180**	**3.40**	**63.11**

Results and Discussion

Analysis of waste soybean oil before and after malenization is given in table no. 1 and table no.3 respectively. Composition of maleic treated waste soybean oil is shown in table no. 2. Microwave synthesis of malenized waste soybean oil is also shown in table no. 4.

Analysis shows that waste cooking oil already has high acid value due to frying and higher percentage of free fatty acids but when it is treated with maleic anhydride, acid value of malenized product increases tremendously about three times[9,10].

The Malenized oils are clear, bright yellow coloured, highly viscous and brilliant product which can be used in specialty electro deposition coatings, water thinable coatings, aqueous emulsion paints, liquid detergents, creams and lotions. As these Malenized oil have a higher acid value they can be neutralize with various alkalis to get water thinable compositions. Polymeric surfactants are an exciting new addition to the existing product range of surfactants.

Present work of modification of waste cooking oil by microwave heating enhances its usability. It can be better alternative for vegetable oil in above applications.

Conclusion

The following conclusions stand confirm from the above research work which is explained as follows.

1. The Following standard conditions can be recommended for Malenization of waste soybean oil.
   - Temperature -125^{0}C, Microwave power -100 watt, Time-4 min
   - Temperature-160^{0}C, Microwave power-160 watt, Time-5 min
   - Temperature-200^{0}C, Microwave power-180 watt, Time-3.40 min

2. Synthesis of Malenized waste cooking oil will increase the usability of the used vegetable origin oil to a very vast extent, the reason for this is,

   a) Reaction is simpler.

   b) Modification requires lesser temperature compared to the alkyd formation from vegetable oils.

   c) Molecular weight of the vegetable oil increases to a very desirable range.

3. There is tremendous time saving in microwave synthesis, The time of reaction is reduced from hours to just few minutes. Thus the same reaction can be carried out in a small reactor with little manpower and risk.

4. The space required for microwave reactor is very small and man power required can be reduced considerably.

5. We conclude that commercial production and use of the Malenized waste cooking oil can solve the problem of environment pollution caused by petroleum products and a Varity of modified oil can be made available for industrial products.

6. The novel findings of this research show good use of waste vegetable or oil into useful products leading the research work towards green chemistry.

References

1. Zini P, "Polymeric additives for high performing detergents" Technomic publication Co inc Lancaster BASEL ; 1995, pp: 15-18.
2. "Encyclopedia of Polymer Science and Technology" John Wiley and Sons 1982 (I Edition) vol-9 Page. No. 182-191.
3. Agrawal R.S., Kakadkar G., Gogte B.B., "Sorbital Based Polymeric surfactant for Detergent Formulation," Soaps Detergent and Toiletries review PP 19-20-25, 2003
4. Patil Pankaj, Gogte B.B., "A Novel Chain Stoppered polymer for detergent Composition," Soaps detergents and Toiletries review, PP 21-25, July 2005.
5. Ansuman M. Bhagwat and Dr. B.B. Gogte, "A Novel Liquid Stain Remover Cum Detergent Based on Rosinated Alkal Polymer," Soap Detergent and Toiletries review, 20-25, Sept 2004.
6. S.K.Kharkate, V. Y. Karadbhajne, B.B. Gogte, "Some resin based ecofriendly liquid detergents," Journal of scientific and Industrial Research, Vol 64, October 2005, PP 752-755.
7. Annual Book of ASTM Standard American society for testing and material, Vol-6.01d, 1639-70. (1981) ASTM standard Method for acid value of organic coating materials.
8. Bayuy A.D.," Polymeric Surfactant and their use in industrial product," Paint India (March 1993) PP. 45-52.
9. Marcel Dekkar "Polymeric surfactant" Surfactant Science series, Vol-42,Inc pp.165-176,203-205.
10. Chao Zhang, Liqiong Liao and Shaoqin (Sarah) Gong, "Recent developments in microwave-assisted polymerization with a focus on ring-opening polymerization" Green Chemistry, 2007, vol 9 pp: 303 - 314.
11. W. H. Gardner and L. H. Felt National Aniline Division Allied Chemical Dye Corporation. Maleic Anhydried In ECT 1st ed., Vol-8 pp. 680-696.

*****