Sunflower seed oil polymerization by ion exchange resins: acidic heterogeneous catalysis

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Sunflower seed oil, like other unsaturated triglycerides, is susceptible to thermal degradation and oxidation. Polymerization is an easy and economical way to decrease the number of double bonds and heterogeneous catalysis and is one of the best choices to produce high quality polymerized oil. In this paper the effect of time, temperature and catalyst concentration on the polymerization reaction is evaluated. As expected, the reaction rate increased in parallel with temperature and catalyst concentration. Time could affect the product properties. Finding the optimum conditions is crucial to control the properties of the polymerized oil. GPC and viscometry techniques were used to control the reaction extent. The product's behavior after polymerization was studied using TGA and FT-IR and its analysis was performed according to ASTM and USP.

INTRODUCTION

The sunflower is a distinctive flowering plant (*Helianthus annuus L.*). The seeds of this plant contain a valuable edible oil that contains more vitamin E than any other vegetable oil.[1-2] Sunflower seed oil finds many industrial applications, e.g. in food, cosmetics, paints, surface coatings, lubricants and surfactants.[3-7]

This oil is a combination of monounsaturated and polyunsaturated fatty acids with low saturated ones.[8] The percentage of saturated fatty acids in the sunflower seed oil is about 5% while it reaches 45% for monounsaturated and 46% for poly unsaturated fatty acids. The total percentage of essential fatty acids (linoleic and linolenic) in sunflower seed oil is more than 50%. These unsaturated long chain fatty acids are useful in improving the low temperature properties of the finally polymerized oil.[9] The number of double bonds per molecule is about 5 and the remarkable point is that all of these double bonds are in "cis" configuration.[10] The chemical and physical properties of the vegetable oils strongly depend on the degree of unsaturation, which can be determined by measuring the iodine value (IV).[11-12]

The fatty acid percent composition of the deodorized sunflower seed oil is as follows: palmitic acid 5-7.6%, stearic acid 2.7-6.5%, oleic acid 14-39%, linoleic acid 48-74%, linolenic acid <0.3%. The specification is shown in *Table 1*.[13-14]

Table 1. Typical properties of sunflower seed oil

No.	Items	Standard
1	Appearance	Yellowish transparent liquid
2	Specific Gravity at 25° C	0.915-0.919
3	Viscosity at 25° C	49 mPa.s
4	Saponification Value	188-194 mg KOH/g
5	Iodine Value	120-140 gI_2/100g
6	Titre	15-18° C
7	Insoluble impurities	~0.05%

High levels of oleic acid make the oil more susceptible to oxidation and hence more unsuitable for processes requiring high oxidative stability at high temperatures as in biodiesel and biolubricant applications.[15-17] To reduce the risk, the double bonds of the oil could be polymerized which is a less expensive approach compared to other methods, e.g. hydrogenation.[18] By controlling the polymerization conditions, the preferred viscosity, color and molecular weight could be achieved for a variety of vegetable oils with a broad range of iodine values and fatty acid compositions.[19]

From macromolecular viewpoint unsaturated oils are monomers with more than one functional group capable of polymerization.[20-21] There are

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two major industrial techniques for oil polymerization: thermal [22] and air blown methods.[23]

In the first process, the oil is simply heated to a temperature of 290-330 °C for 20-30 h with or without an inhibitor like antraquinone to control the molecular weight of the polymer. The reaction is time consuming and the product is a yellowish viscous liquid. The long time of the reaction is due to the low reactivity of non-conjugated double bonds in the oil structure.[24-25]

In the second one, the oil is heated to 100-110 °C for 30-50 h while air is purged in it. Many functional groups in the oil structure are oxidized under these conditions to ketones, aldehydes, hydroperoxides and carboxyl which are hazardous for human health.[26-27]
Cationic polymerization could be easily completed on the internal double bonds bearing alkyl electron donating substituents of unsaturated oils such as sunflower seed oil.[28-32] There are many reports in the literature for cationic polymerization of the double bonds in acidic conditions using homogenous catalysts, e.g. superacids [33] ($H_2S_2O_7$) or Lewis acids [34] (BF_3 and $TiCl_4$), and also heterogeneous ones like clay and zeolite.[35-36]

The aim of this paper was to use ion exchange resins as heterogeneous polymer-based catalysts to polymerize sunflower seed oil. Compared with others, they are high-capacity macroporous catalysts which could regenerate and tolerate severe conditions without degradation.[37] They showed more efficient and economical than acid catalysts and the reaction was performed in milder conditions than the previously reported unsaturated oil polymerization. The reduction of the double bonds is demonstrated by the decrease in iodine value from 120-140 to 70-90 g I_2 100 g^{-1}.
The main economical advantage of using these catalysts is the simplicity of their isolation from the reaction mixture which makes the reaction a short time experience in comparison to similar processes. The optimum conditions were found by varying the reaction parameters such as time, temperature and concentration of catalyst. The polymerized oil was finally analyzed.[38]

EXPERIMENTAL

Materials

The used sunflower seed oil was commercially deodorized oil obtained from TEXTRON (Spain) with the specification of Table 1. A commercial strongly acidic polystyrene ion exchange resin was used as heterogeneous catalyst under the brand name of AMBERLITE™ FPC23 H from Dow Company. The total exchange capacity of the resin was 2.2 eq L^{-1}. Sulfonate functional groups were activated before the reaction while the final H^+ content of 0.056 eq. was used in the reaction. All other materials were prepared from technical grade products of Merck Company.

Apparatus

The polymerization was carried out in a 2 liter 3-neck round bottom flask with mechanical overhead stirrer, thermometer, electrothermal heating mantle and nitrogen line to remove oxygen from the reaction mixture. The stirrer was equipped with a stainless steel shaft and four anchor-shaped stirrer blades in two different heights, one at the end of the shaft and the other in the lower one-third of it. There were also four small metallic mesh bags attached to the end of each blade filled with activated heterogeneous catalyst.

Reaction procedure

The sunflower seed oil (1000 g) was weighed in the flask (same amount in every reaction) equipped with stirrer, heating mantle, thermometer, nitrogen line to sparge nitrogen and filled bags of activated heterogeneous catalyst.[38] The reaction was performed at three different temperatures by controlling the temperature of the heating mantle at 60-90-150 °C. To find the best time, samples were withdrawn at different times from t=0 to t=11 h every 30 min. The catalyst concentrations were varied as 1.7, 1.9, 2.2, 2.5, 2.7 eq (per liter of oil). Pure nitrogen gas was purged in the reaction by a sparger with a rate of 5 mL min^{-1} to prevent oxidation of the oil. At the end of the reaction time the product was evacuated from the flask and analyzed without any further purification.

Analytical procedure

Gel permeation chromatography:

Gel permeation chromatography was performed on a Shimadzu Class-LC10 GPC Prominence Model instrument. The stainless steel column with length of 300 mm and internal diameter of 7.7 mm was packed with high performance spherical gel made of styrene-divinylbenzene co-polymer with diameter of the particles: 5 *p,* pore size: 100 A of the equivalent in term of exclusion power and resolution. The column temperature was increased from room temperature to 60 °C with a rate of 5 °C 10 min^{-1}. The column was stored in toluene. A refractive index detector with a sensivity at full scale at least 2 of refractive index was used. Flow

rate was 1 mL min^{-1} and the eluent was tetrahydrofuran.

Viscometry

The extent of the reaction was monitored by viscometry on an Anton-Paar SVM 3000 viscometer at room temperature. This viscometer measures the dynamic viscosity according to ASTM D-7042.[39]

Thermogravimetric Analysis

Thermogravimetric analyzer TGA-DTA, model Diamond TG/DTA, Perkin Elmer Instruments was used. Measurements were performed under N_2 purge. Typically, 5-10 mg of sample were placed in a platinum pan and heated from 30 °C to 600 °C, at 10 °C min^{-1}.

RESULTS AND DISCUSSION

As expected, the sunflower seed oil polymerized in acidic conditions. After 20-30 min the color of the reaction mixture turned a little darker due to the formation of conjugated carbocations with double bonds. The various parameters such as time, temperature and concentration of catalyst were changed to find out the optimum conditions. Some physical characteristics of the finally obtained polymerized oil were determined. Gel permeation chromatography (GPC) and viscometry were used to follow up the reaction extent.

Effect of time on the reaction

Sampling of the reaction mixture and analysis by GPC showed the effect of time on the molecular weight (MW) which was low in the starting point. With time oligomers were formed (Fig. 1). About 10 wt % of the starting oil consisting of saturated fatty acids, e.g. stearic and palmitic acids will be unchanged.

The time effect was also followed by changing the viscosity of the reaction mixture. As demonstrated in Fig. 2, at t = 90 °C, the viscosity gradually increased in the first 4 h of the reaction but after that the viscosity growth was considerable. After 10 h the viscosity of the reaction mixture increased to around 20 Pa.s at 25 °C which is the desired viscosity. It is noticeable that the viscosity of the sunflower seed oil is 0.05 Pa.s at this temperature. As the desired viscosity was achieved for 10 h, this was considered as the optimum reaction time.
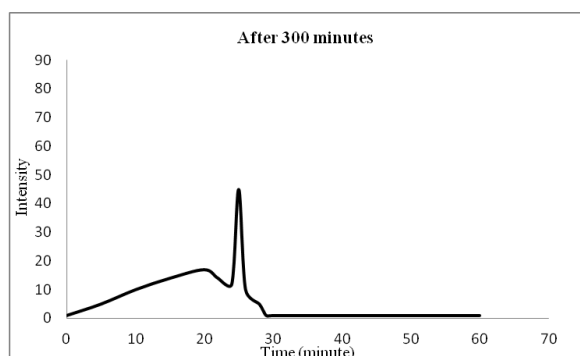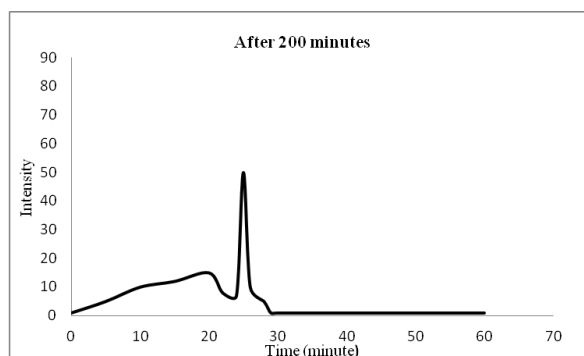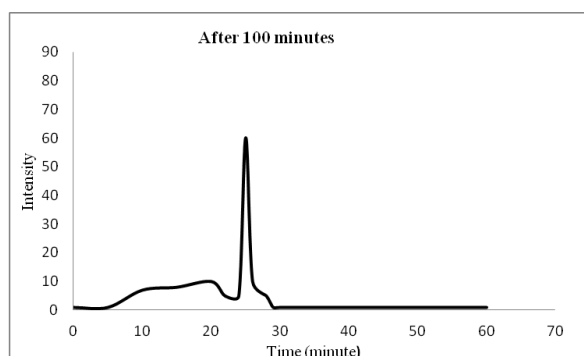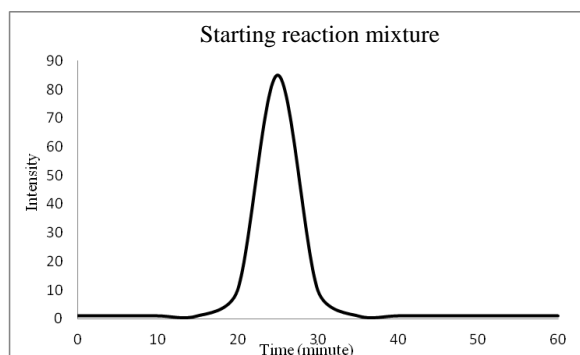

Fig. 1. GPC chromatograms of the reaction mixture at different times after the starting point. (reaction conditions as described in the experimental section).

Effect of temperature on the reaction

To study the effect of temperature on the reaction duration, the catalyst concentration was fixed at 2.2 eq H$^+$ per liter of oil. The viscosity of the samples measured at different temperatures is shown in Fig. 2; the viscosity around 20 Pa.s was

considered to determine the optimum temperature. Compared to 60 °C, the reaction at 90 °C is rapid. By heating the reaction rate will go up; the reaction mixture will be solid at temperatures above 150 °C (Fig. 2). Considering high utility cost in the industry and the easier rate control of the reaction to prevent runaway, the t=90 °C was determined as the optimum temperature.
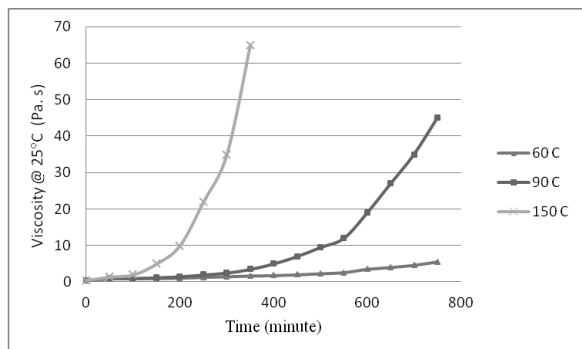

Fig. 2: Effect of reaction temperature on the viscosity of the product with time. (reaction conditions as described in the experimental section).

For preparing a more viscous product, higher temperature and longer time should be used [40-41].

Effect of catalyst concentration on the reaction

The reaction rate dependency on catalyst concentration was studied at 90 °C and catalyst concentrations of 1.7, 1.9, 2.2, 2.5, 2.7 eq (per liter of oil) were used to reach viscosity around 20 Pa.s. Actually the viscosity was used as an indication of the reaction extent. The results are demonstrated in Fig. 3. It is obvious that the reaction time was shortened proportional to the increase in catalyst concentration. If the chosen concentration was more than 2.2 eq. per liter of oil there was no noticeable increase in the reaction rate. Considering the high price of these catalysts, the concentration of 2.2 eq H^+ per liter oil was selected. In other words, the used catalyst was 25.5 mL per liter of oil which equals to 2.2 eq L^{-1}.[37]

Physical properties of the polymerized oil

At the end of the reaction (t=10 h, T=90 °C and catalyst concentration= 2.2 eq H^+ per liter oil), the polymerized oil was evacuated and some characteristics of cationic polymerized soybean oil were analyzed according to ASTM and USP.[42] (*Table 2*). The results were in the mentioned range of the polymerized oils.[43]
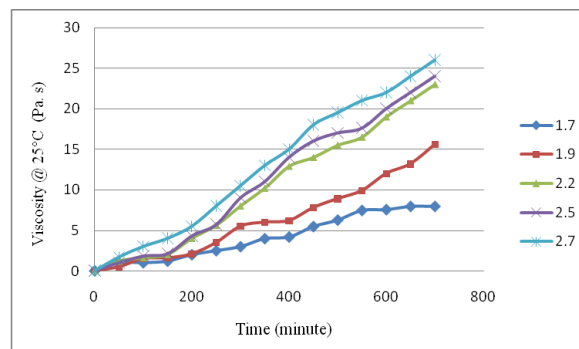

Fig. 3. Effect of catalyst concentration on the viscosity of the product with time. (reaction conditions as described in the experimental section).

Table 2. Characteristics of polymerized oil obtained from cationic polymerization after 10 h at T=90 °C and catalyst concentration of 2.2 eq H^+ per liter oil.
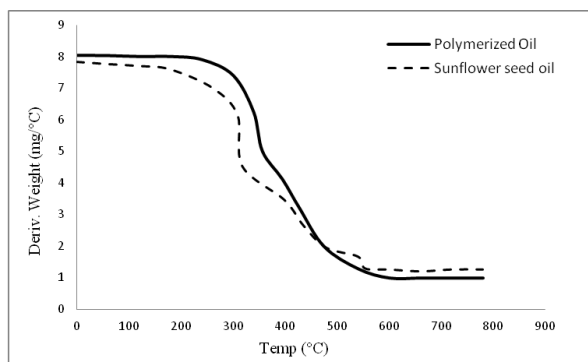
Items	Results	Analytical Method
Appearance	Yellowish Viscous Liquid	-
Color (Gardner)	Max. 7	ASTM D1544
Acid Value, mg KOH/g	Max. 5	ASTM D2076
Peroxide Value, meq/Kg	Max. 5	USP33-NF28
Saponification Value, mg KOH/g	82-90	ASTM D5558
Iodine Value, mg I_2/100g	70-90	ASTM D1959
Moisture	Max. 0.5%	ASTM E203
Insoluble impurities	Max. 0.1%	
Viscosity, 25 °C, Pa.s	17.52	ASTM D445
Average Molecular Weight	1900-2100	-

Thermal characterization of the sunflower seed oil compared to polymerized oil
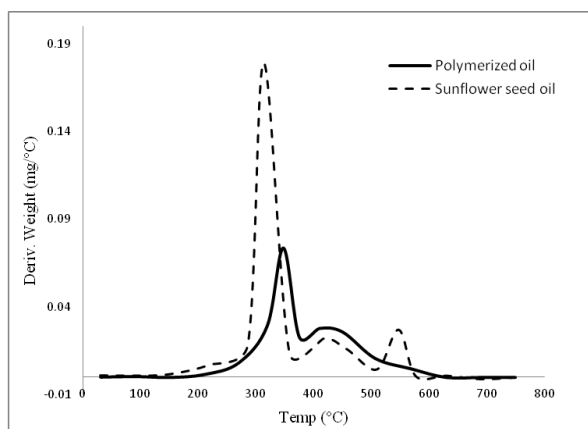
Thermal degradation was studied by means of thermogravimetric analysis (TGA). TGA tests were conducted for sunflower oil from ambient temperature to 800°C at a heating rate of 10°C/min in nitrogen environment with a flow rate of 100ml/min. By heating the oil was decomposed to aldehyde, ketones and alcohols which are volatile so the weight decreased [44, 45]. Figures 4a and 4b show the TGA curves and their derivatives. As can be seen in the figures, the thermal decomposition of sunflower seed oil occurs in three stages (peak

maxima at 314°C, 417°C and 547°C), related to the decomposition of polyunsaturated, monounsaturated and saturated fatty acids. The first step is the most vital one for the thermal stability of the oil, because this is the step where decomposition of the unsaturated fatty acids starts.

Polymerized oil shows two main peaks (peak maxima at 347 °C, 450 °C), attributed to different stages of the decomposition process and polymerization degrees. As expected, the thermal stability of the polymerized oil is higher than that of the raw oil.
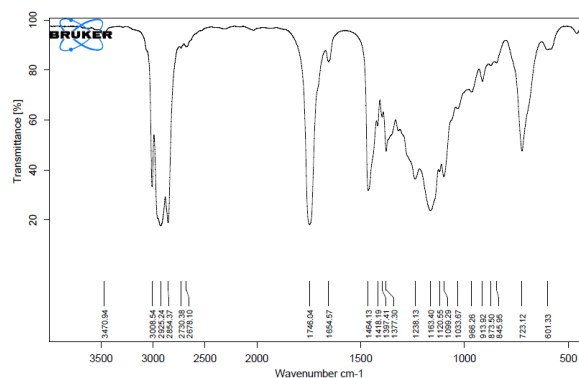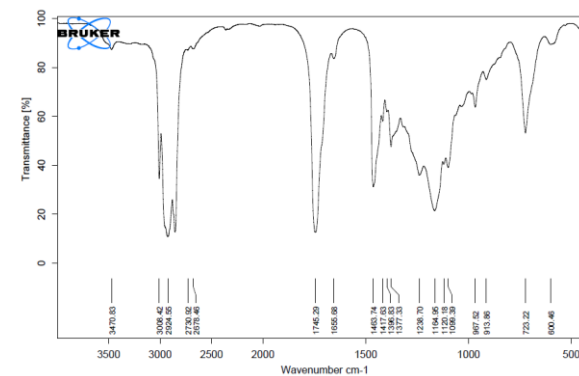

(a)

(b)

Fig. 4. TGA thermograms for sunflower seed oil and polymerized oil.

FT-IR spectra of polymerized oil compared to sunflower seed oil

The FT-IR spectra of sunflower seed oil and polymerized oil are shown in Figures 5a and 5b. The band around 3000 cm^{-1} was assigned to the CH vibrations of CH, CH$_2$ and CH$_3$ groups in the two samples. The carbonyl groups displayed a sharp band at 1745 cm^{-1}[46]. It is worth noting that the 967 cm^{-1} band in the polymerized oil spectrum was attributed to the trans double band while this band did not appear in the sunflower seed oil spectrum. This indicates a transformation of the cis to trans double bands during acid catalytic polymerization.

(a)

(b)

Fig. 5. FT-IR spectra of sunflower seed oil (a) and polymerized oil (b).

CONCLUSION

The polymerization reaction of sunflower seed oil by AMBERLITE™ FPC23 as a heterogeneous catalyst was investigated in a stirred batch reactor. The reaction mixture behavior was controlled by gel permeation chromatography and viscometry. The increase of viscosity with time is a direct measure of the efficiency of the process used for cationic polymerization of sunflower seed oil. The suitable conditions were: 90 °C, 10 h and catalyst concentration of 2.2 eq per liter of oil to reach a viscosity of the polymerized oil of around 20 Pa.s. The advantages of using these mild reaction conditions to other available methods are: low temperature, shorter time and no need for purification of the product after the reaction.

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ПОЛИМЕРИЗАЦИЯ НА СЛЪНЧОГЛЕДОВО МАСЛО С ЙОНООБМЕННА СМОЛА: КИСЕЛИНЕН ХЕТЕРОГЕНЕН КАТАЛИЗ

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(Резюме)

Слънчогледовото масло, както другите ненаситени триглицериди е чувствително към термично разлагане и окисление. Полимеризацията е лесен и икономичен начин да се намали броя на двойните връзки, а хетерогенният катализ е един от най-добрите способи за получаването високо-качествено полиемризирало олио. В тази работа са оценени ефектите на времето, температурата и концентрацията на катализатора върху полимеризацията. Както се очаква, скоростта на реакцията се повишава успоредно с температурата и концентрацията на катализатора. Времето влияе върху качествата на продукта. Оптималните условия на процеса са от ключово значение за контрола върху свойствата на полимеризралото олио. За тази цел са използвани гел-проникваща хроматография и вискозиметрия. Отнасянията на продукта след полимеризация са изследвани с помощта на термо-гравиметричен анализ и инфрачервена спектрофотометрия (FT-IR), както данните са интерпретиране според стандартите ASTM и USP.