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Application of Alkyd Resins Based on All Organic Substances in the Glycerol Phase from Biodiesel Production

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Abstract: ***For the purposes of the present work, the glycerol phase, that is separated as side product from the biodiesel production from cooking oil was used. After its treatment with acid, two liquid fractions were obtained - crude glycerol and organic matter. These two fractions were used to obtain two kinds of alkyd resins by the method of alcoholysis, heating was by microwaves. Obtained alkyd resins were used in formulation of white paints as binding substance. It was found that the main characteristics,like adhesion, flexibility, drying duration and chemical resistance, of the samples were comparable to these of the samples of standard soy paint and could successfully be used when the requirements towards color brightness are not high.***

Keywords: waste cooking oil, biodiesel,microwaves, utilization

1. Introduction

Alkyd resins could bemodified by adding fatty acids and other components. The inclusion of fatty acids imparts aptitude towards formation of flexible coating.Properties of the alkyd resins depend on a great extent of the type of the fatty acids. There are data in the literature about the preparation of alkyd resins using flax, sunflower, soy, palm and ricin oil [1], fatty acids of sunflower oil[2,3], organic matter present in the glycerol phase obtained from the biodiesel production from sunflower [4,5] and rapeseed oil[6], etc.

However, no data was found in the literature about preparation of alkyd resins, modified with the organic matter in the glycerol phase obtained from waste cooking oil[7-10]. The quantity of the other matter organic non-glycerol (MONG) is usually 15-35% and their utilization is of great ecological and economic importance. The MONG composition is complex and variable and the glycerol phase undergoes certain treatment to simplify it. It has been reported in the literature [4-6] about preliminary saponification of the glycerol phase to convert all the organic non-glycerol matter to fatty acids. By the biodiesel production, however, the big installations contain production units for purification of the glycerol phase and this purification involves only treatment with mineral acid without preliminary saponification. This is a sound reason to search for ways to utilize the glycerol phase treated by this method.

In the present work, for the first time the possibility to prepare alkyd resins and alkyd paints from all the organic matter obtained after treatment with mineral acid without preliminary saponification is considered. Besides, for the first time the initial raw material, which the application of the alkyd resins depends on, is waste cooking oil.

2. Materials and Methods

Materials

Refined sunflower oil (RSO) and waste cooking oil (WCO) were supplied by local eating establishment. Glycerol phase (GPh) was laboratory prepared after transesterification of WCO with potassium methoxide. Potassium hydroxide (KOH), phthalic anhydride (PhA),xylene, LiOH, calcium, cobalt and zirconium dryers, Anti-Terra-U and methyl ethyl ketoxime (MEKO) were purchased from Aldrich. Technical grade titanium (IV)oxide,calcium carbonate and white spiritwere obtained from commercial sources and used without further purification.

Preparation and treatment of the glycerol phase

WCO was purified as follows:0,4 g zeolite are added to 210gWCO. The adsorption is carried out for 2 hours at 100°C. In 1 L flask, 200 ml methanol and 3 g KOH were placed. After their complete dissolution, the treated WCO was added. The transesterification was carried out at 60°C using microwaves.

The glycerol phase was separated from the biodiesel phase and concentrated $H_3PO_4$was added until pH=3. Solid state formed which was separated by decanting. Methanol was separated from the liquid phase. The mixture obtained was placed in a separating funnel and left for 17 h. two liquid fractions were obtained. The light one was the organic fraction (OF). The heavy one contained mainly glycerol. It was neutralized with KOH and called CG.

The two fractions were analyzed. Methanol and the methyl esters of the fatty acids (FAMEs) were determined by GC with FID detection.The contents of glycerol, water, MONG, ash content, color by Gardner, acid value and density were determined using standardized methods of analysis, as described in [7].

Synthesis of the alkyd resins AR1 and AR2

The necessary amount of CG was placed in a one-neck flat bottomed flask of 500 ml. the flask was placed in a microwave reactor DAEWOOKOR 6485 and the temperature was kept 100°C until complete evaporation of the water. Then, the determined amount of OF is added, as well as 2 % LiOH, and the temperature was raised to 180 - 200°C.The interaction was monitored by measuring the acid value(AV). When this value decreased below 10 mgKOH/g, the glycerolysis was assumed to be completed.

The reaction mixture was then cooled to 150°Cand the necessary amount of phthalic anhydride was added under continuous stirring. The temperature was gradually raised to 240°C.The process was monitored by measuring the acid value.

The reaction was terminated at AV<10 mg KOH/g. The alkyds were cooled to 70°C and xylene was added to them to achieve the necessary consistency. The alkyd resins obtained were then hot filtered which removed the potassium phosphate.

Preparation and estimation of the alkyd resin paints AR1 and AR2

30 g of alkyd resin was mixed with the whole amount of pigment (24 g of titanium dioxide). A thick pale gray paste was obtained. Then a solvent (16 g of white spirit), a dispersing agent (0,3 g of Anti-Terra-U) and a thickener (5 g of calcium carbonate) were added. After complete homogenization (about 30 minutes), 25 grams of alkyd resin were added to the resulting paste until good flowability of the paint was obtained. Finally, the hardeners and anti-skinning agent (0,3 g MEKO) were added.

This procedure was performed for both alkyd resins with varied amount of driers aiming to find their optimal values.

Each of the paints obtained was uniformly applied on a glass or tin plate placed horizontally and allowed to dry at room temperature. Some basic characteristics of the films prepared from AR1 and AR2 were estimated as described in [1].

3. Results and Discussion

The initial material used in the present study was glycerol phase (GPh). The studies showed that it consisted of: glycerol -40,2 %; water -12,2 %; methanol – 16,5%; MONG(soaps, biodiesel, mono-, di- and triglycerides) -25%; ash- 6,1%. Besides, the density was determined to be ρ = 1,09g/cm^{3}andpH= 10. In this state, the GPh cannot be utilized. To simplify its composition, it was acidified with concentrated H_3PO_4until pH=3 was measured. By this treatment of the GPh, the following interactions occur. При това третиране наGP, протичат взаимодействия със:

- With soaps, which gives higher free fatty acids (FFA)
- KOH excess, which gives solid phase (potassium phosphate salts).

After certain period the salts precipitate and for the purposes of the present work they were separated by decanting of the liquid phase. Potassium phosphate can be used as fertilizer.

The liquid phase obtained consisted of glycerol, water, methanol,FFAs, FAMEs, mono, di- and triglycerides, traces of potassium phosphate and phosphoric acid. After evaporation of methanol, the mixture obtained was placed in separating funnel. Two layers were obtained:

- Upper layer (OF) consisting of FFAs, FAMEsand glycerides;
- Lower layer consisting of glycerol, water, traces of potassium phosphate and phosphoric acid.After neutralization with KOH solution in ethanol followed by evaporation of the ethanol, the so called crude glycerol (CG) was obtained.

Using standardized methods of analysis, the basic characteristics of the CG and OF obtained were determined (Table 1)

Table 1: Basic characteristics ofCGand OF)

CG		OF	
Characteristics	values	Characteristics	values
Specific gravity	1,152	Specific gravity	0,937
Gardner color	9	Gardner color	6
Glycerol content, wt.%	80,2	Yield of OP, %	24
Water content, wt.%	11,4	FFAs, wt.%	54,8
MONG content, wt.%	2,5	Esters, wt.%	44,3
Ash content, wt.%	5,9	Others, wt.%	0,9

It can be seen (Table 1) that the glycerol content in CG increased to 80, 2%. Among impurities, the highest content was that of water which can be easily removed by evaporation. The ash content was mainly due to potassium phosphate while MONG consisted of compounds which had not been well separated from the OF. The OF consisted of mainly FFAs andFAMEs. The total quantity of the other compounds – mono-, di and triglycerides was quite small – less than 1 %.

An analysis of the fatty acids present in the OF was carried out by the method of gas chromatography with FID. The following results were obtained: C18:0(12,7%); C18:1(27,2%); C18:2(52,2%) C18:3(0,0%). These data were compared to the results obtained for the composition of the FFAsinRSO before its use for frying: C18:0(3,7%); C18:1(25,2%); C18:2(63,2%) C18:3(1,2%). It can be seen that the Bquantities of the stearic and oleic acids increased in OF while these of the polyunsaturated fatty acids (linoleic and linolenic acid) decreased. It means that processes of saturation of mainly the polyunsaturated double bonds occur during the thermal treatment.

This result was confirmed by the iodine value (I.V.) which indicates for the degree of unsaturation of the fatty acids.It was determined that the iodine value of OF was I.V.=104 gI2/100 g. This value is significantly lower than that for RSO, I.V.=130 gI2/100gand confirmed the occurrence of processes of saturation of the double bonds in the waste cooking oil.

Preparation of the alkyd resins AR1 and AR2

Two kinds of alkyd samples – short oil and medium oil were obtained from OF, CG and phthalic anhydride. To prepare good quality alkyds and avoid gelation, their composition os first theoretically calculated (Table 3.). By the determination of the alkyd composition, it was taken into account that the OF consisted of 54,8% FFAsand 44,3% FAMEs; the content of G in CG was 80,2%; the introduction of CG adds 2,5% MONG.

Table 3: Compositions of the alkyds

Initial materilas(g)	AR1	AR2
OP	35	48
G	25	25
CG	31	31
PhA	30	30

The alkyds were obtained by the monoglycerides method. The glycerolysis begins immediately after the evaporation of the water which is the main impurity in CG. During the first 20 min the temperature was kept 180°C for the FAMEs glycolysis to proceed. Then, the temperature was raised to 200°C for the glycolysis of the fatty acids (Scheme 1).

Scheme 1. Glycerolysis of FAMEsand FFAs

The process of glycerolysis gives mainly monoglycerides and small quantities of di- and triglycerides.Simultaneously, he low molecular weight compounds H_2O and CH_3OH are produced. The microwaves have the ability interact with H_2O and CH_3OH which results in shifting of the equilibrium to higher yield. The mono- and diglycerides contained in small quantities if the OF can also take part in the glycerolysis process but it doesn't lead to changes in the composition of the end product of the glycerolysis. The process was monitored by measuring the acid value. Its duration was 50 min.

The second stage is the glycerides esterification with phthalic anhydride. The process starts at temperature of 170°C and it increases to 240°C with the increase of viscosity. The process is monitored by measuring the acid value and continued for 80 min for AR1 and 90 min for AR2.

After the completion of the esterification, the alkyds were cooled to 70°C and solvent xylene was added to them to achieve consistency good for deposition. The alkyd resins obtained were then hot filtered to remove the last contaminating substance – potassium phosphate.

Preparation and study of the alkyd paints AP1 and AP2

The alkyd resins AR1 and AR2 were introduced in the compositions of the alkyd paints AP1 and AP2 as binding substances. The method for preparation of the alkyd paints is described above. The hardeners used in the paints were as follows:

♦forAP-1: Calcium drier (0,8g), Cobalt drier (0,2 g) and Zirconium drier- (0,8 g),

♦ заAP-2: Calcium drier (0,9 g), Cobalt drier (0,1 g) and Zirconium drier- (0,9 g).

Some basic characteristics of AP1 and AP2 were determined (Table 3). For comparison, data obtained by Isaac et al.[1] for standard alkyd paint manufactured on the basis of soya oil are also included in the table.

Table 3: Some basic characteristics of AP1 and AP2 and standard soybean paint

Characteristic	AP1	AP2	Standard soya paint sample[1]
Colour	very light blonde	very light blonde	white
Solidcontent (%)	67,91	71,55	65,01
Density, g/cm^3	1,13	1,15	1,14
Set- to- touch time, min	10	15	6
Dry – through time, min	400	600	360
Adhesion	excellent	excellent	excellent
Flexibility	excellent	excellent	excellent
stability to immersion in water	a	a	a
Chemical resistance to: ♦NaCl, ♦5% solutionH_2SO_4, ♦0,1 mol KOH	 a a c	 a a c	 a a b
a – no change; b – opaque film; c - partially dissolved film			

It can be seen (Table 3) that the basic characteristics of the samples of AP1 and AP2 were comparable to that of the standard paint prepared on the basis of soya oil and can successfully be used in the formulations of paints for which the requirements for color brightness are not so strong.

4. Conclusion

A possibility for utilization of all the organic substances in the glycerol phase produced by biodiesel production from waste cooking oil was considered. It is shown that the two organic fractions (glycerol and organic) obtained after treatment with mineral acid (without preliminary saponification) can be used as initial materials for production of alkyd resins. The latter can successfully be used as binders in the formulations of paints for which the requirements for color brightness are not so strong.

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