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Phenolation of vegetable oils

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Abstract: Novel bio-based compounds containing phenols suitable for the synthesis of polyurethanes were prepared. The direct alkylation of phenols with different vegetable oils in the presence of superacids (HBF_4 , triflic acid) as catalysts was studied. The reaction kinetics was followed by monitoring the decrease of the double bond content (iodine value) with time. In order to understand the mechanism of the reaction, phenol was alkylated with model compounds. The model compounds containing one internal double bond were 9-octadecene and methyl oleate and those with three double bonds were triolein and high oleic safflower oil (82 % oleic acid). It was shown that the best structures for phenol alkylation are fatty acids with only one double bond (oleic acid). Fatty acids with two double bonds (linoleic acid) and three double bonds (linolenic acid) lead to polymerized oils by a Diels–Alder reaction, and to a lesser extent to phenol alkylated products. The reaction product of direct alkylation of phenol with vegetable oils is a complex mixture of phenol alkylated with polymerized oil (30–60 %), phenyl esters formed by transesterification of phenol with triglyceride ester bonds (<10 %) and unreacted oil (30 %). The phenolated vegetable oils are new aromatic–aliphatic bio-based raw materials suitable for the preparation of polyols (by propoxylation, ethoxylation, Mannich reactions) for the preparation of polyurethanes, as intermediates for phenolic resins or as bio-based antioxidants.

Keywords: vegetable oils; phenol; alkylation; aromatic electrophilic substitution; cationic polymerization.

INTRODUCTION

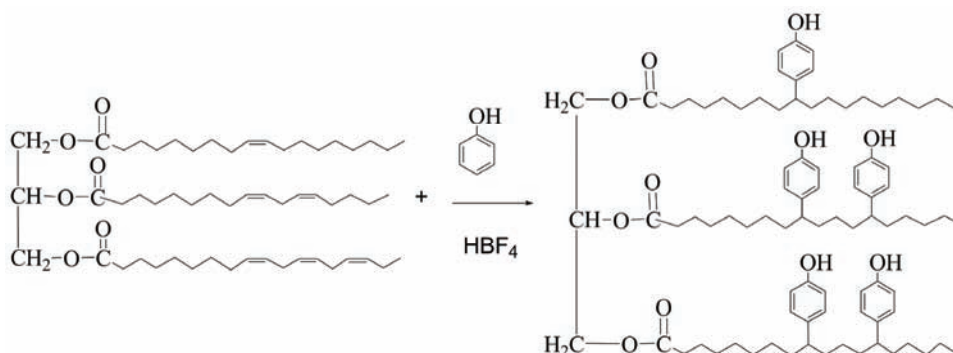
The constant quest for new materials from renewable resources is driven by environmental and sustainability concerns. Vegetable oils are one of the most important groups of renewable raw materials because they are relatively inexpensive and allow a range of chemical reactions at double bonds, ester groups and

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allylic positions. Vegetable oils having hydroxyl groups and phenyl rings are multifunctional components useful for the preparation of polyurethanes and phenolic resins. They can be prepared economically in one step by Friedel–Crafts alkylation of phenols with different oils or fatty acids. The objective of this work was to study the feasibility of the preparation of phenolated oils, determine the reaction conditions for the highest yield and examine the reaction mechanism. Particular attention was paid to the side reactions occurring simultaneously with the phenol alkylation reaction.

The internal double bonds in vegetable oils are of low reactivity, thus the introduction of different functional groups is necessary to create useful monomers for polymerization.^{1–8} The double bonds of fatty acids can be observed as 1,2-disubstituted olefins.^{1–7} Due to the electron-releasing alkyl groups, they are relatively rich in electrons and capable of reacting with electrophilic species, such as protons, carbocations and free radicals. The Friedel–Crafts alkylation of phenols with olefins is a well-known reaction used on an industrial scale for the production of many important chemicals, including a range of antioxidants by alkylation of phenols with isobutylene, octene, diisobutylene, propylene trimers (nonene) and tetramers.^{9–12} The ethoxylated long chain alkylated phenols represent one of the most important class of nonionic surfactants (*e.g.*, ethoxylated nonyl phenol).¹³ Using this general concept, the Friedel–Crafts alkylation of phenol with vegetable oils, in the presence of acid catalysts was investigated in this study (Scheme 1).



Scheme 1. Friedel–Crafts alkylation of phenol with soybean oil (ideal reaction pathway).

The idea of phenol alkylation with vegetable oils or derivatives of vegetable oils (fatty acids, fatty acid methyl esters, *etc.*) is not new. Generally, the alkylation of phenol with free fatty acids are preferred.^{12,14–23} Direct alkylation of linseed oil with phenol or cresols in the presence of triflic acid and the use of the alkylated product for the synthesis of modified phenolic resins is described in a patent.¹⁵ The first direct alkylation of phenol with soybean oil was also des-

cribed.¹ Neither the patents nor the publications gave detailed information about the mechanism, side reactions, composition of the molecular species in the alkylated product or the reactivity of the double bonds.

EXPERIMENTAL

Materials

Refined, bleached and deodorized (RBD) soybean oil (SBO) supplied by Cargill had an iodine value (*IV*) of 129 g I₂/100g. High oleic safflower oil (HOSO) having 82 % oleic acid and an *IV* of 85 g I₂/100g was supplied by Cargill (Minneapolis, MN, USA). Triolein was purchased from NU-CHEK Prep. Inc. (Elysian, MN, USA) and 9-octadecene, purity 97 %, was purchased from Alfa Aesar (Ward Hill, MA, USA). Methyl oleate, purity >99 % and methyl linoleate, purity >99 %, were purchased from NU-CHEK Prep, Inc. Phenol (purity 99 %), melting point (m.p.) 40–42 °C, tetrafluoroboric acid (HBF₄) as a 54 % solution in diethyl ether, and trifluoromethanesulfonic (triflic) acid (CF₃SO₃H) of purity 99 % were purchased from Aldrich (St. Louis, MO, USA).

Methods

The *IV* was determined by the Hanus method.²⁴ The molecular weights (MW) and MW distribution were determined using a Waters gel permeation chromatograph (Waters Corporation, Milford, MA, USA) consisting of a 510 pump, 410 differential refractometer and a data collection system. Tetrahydrofuran (THF) was used as the eluent at 1.00 mL min⁻¹ at 30 °C. Four Phenogel 5 μm columns (50, 100, 1000 and 10,000 Å) plus a Phenogel guard column from Phenomenex (Torrance, CA, USA) covering a MW range of 10²–10⁶ were used. The concentration of investigated compounds in THF was 5 %.

The viscosity was measured at 25 °C on a Rheometrics Scientific Inc. (Piscataway, NJ) SR-500 dynamic stress rheometer, with parallel plates of 25 mm in diameter and gap of 0.2 mm. The infrared spectra were recorded with a Perkin Elmer FTIR Spectrometer 1000 (Waltham, MA, USA)

The ¹H-NMR and ¹³C-NMR spectra were recorded with a 7.05 Bruker Avance DPX-300 NMR spectrometer (Bruker, Rheinstetten, Germany) using 10 % solutions of the investigated compounds in deuterated chloroform (CDCl₃). Eight scans for the ¹H-NMR spectra and 1000 scans for the ¹³C NMR spectra were used.

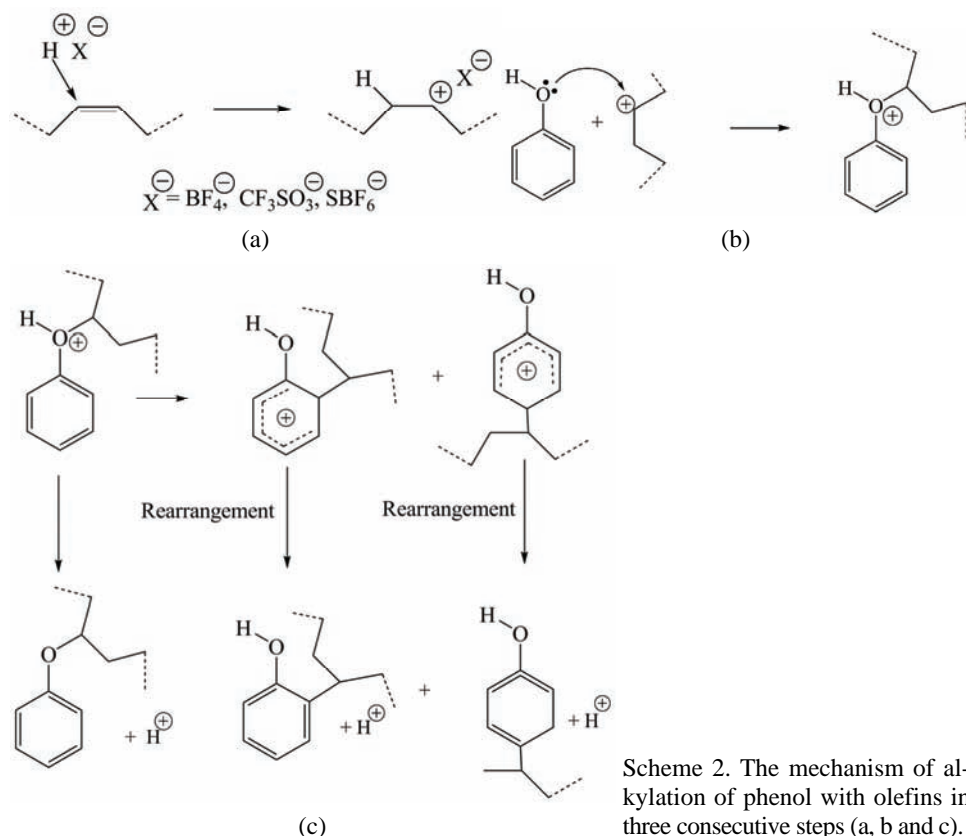
Phenolation reaction

SBO or model compounds (9-octadecene, methyl oleate, HOSO or triolein) were mixed with molten phenol under nitrogen at 50–60 °C. The molar ratio of phenol to double bonds was 1:1. The catalyst was added to the reaction mixture (1 % w/w) and the reaction was maintained for 4–6 h at 90 °C under nitrogen. The reaction mass became red–brown and after 10–20 min a marked increase in the viscosity was observed. The final product was a red–brown viscous liquid. The unreacted phenol was removed by high vacuum distillation.

RESULTS AND DISCUSSION

The accepted general mechanism of the alkylation of phenols with olefins consists of three steps.^{10,11,16,25–28} In the first step, a proton from the catalyst attacks a double bond forming a carbocation (Scheme 2a). In the second step, the phenolic hydroxyls, the most nucleophilic groups in the reaction system, react with the carbocation generated in the first step, giving a protonated phenyl ether

(Scheme 2b). In the third step, the protonated phenyl ether rearranges to the *ortho* and *para* alkylated phenol and to a small extent to the non-protonated free phenyl ethers (Scheme 2c).^{10,27,28}



Scheme 2. The mechanism of alkylation of phenol with olefins in three consecutive steps (a, b and c).

The *IV* gives direct information on the disappearance of double bonds. The changes of *IV* with time during the reaction of soybean oil with phenol and in the absence of phenol are shown in Fig. 1. The decreasing *IV* with SBO only is the consequence of the polymerization reaction, but the much stronger decrease of *IV* in the presence of phenol is direct proof that the alkylation reaction has occurred.

A strong decrease in the double bond content and the appearance of alkylated phenol products in the reaction of SBO with phenol was observed in the ¹H-NMR spectra. The peaks at 5.2–5.8 ppm, characteristic of double bond protons, which were very strong in the soybean oil (Fig. 2), become very small after the reaction of soybean oil with phenol (Fig. 3). Figure 3 also displays peaks at 6.7–7.4 ppm, characteristic of the protons of the phenol ring alkylated at various positions, again indicating that the alkylation of phenol had occurred. A strong de-

crease of mono-allylic protons of SBO at 2.0–2.1 ppm and of bis-allylic protons at 2.7–2.8 ppm can also be seen in Fig. 3, proving their participation in the process.

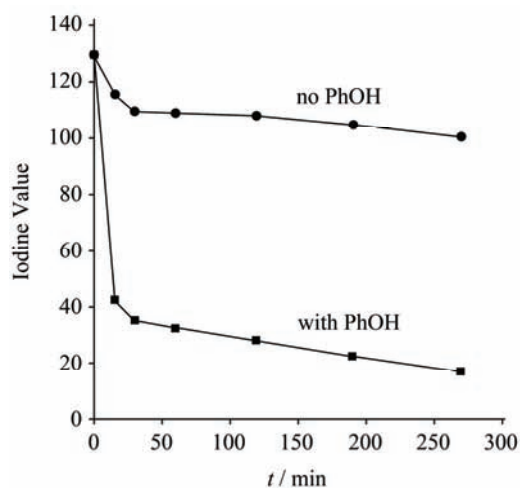


Fig. 1. Variation of iodine value of oil in the absence and the presence of phenol. Catalyst: HBF_4 (1 %); $T = 90^\circ\text{C}$.

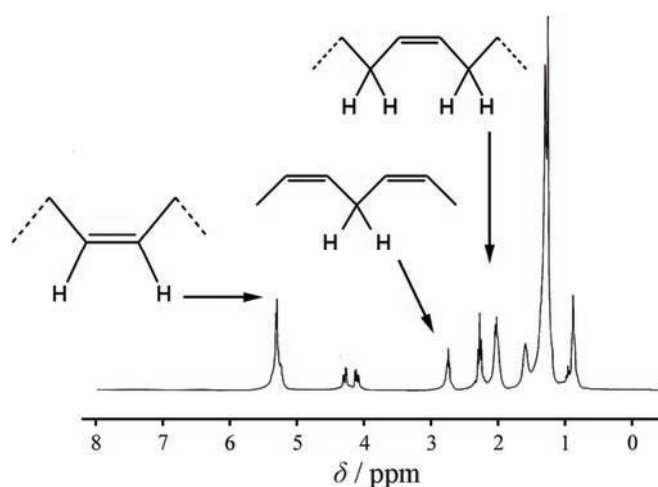


Fig. 2. ^1H -NMR Spectrum of soybean oil.

The ^{13}C -NMR spectrum of the phenolated products displayed specific peaks at 132.2 and 127 ppm, characteristic of carbon atoms from the aromatic rings alkylated in the *para* and *ortho* positions, respectively.

A strong (300–550 times) increase in the viscosity at 25°C of the reaction mass during the phenolation reaction of SBO, from initial values of 0.06 Pa s to 19–33 Pa s after 5–6 h of reaction at 90°C , is illustrated in Fig. 4.

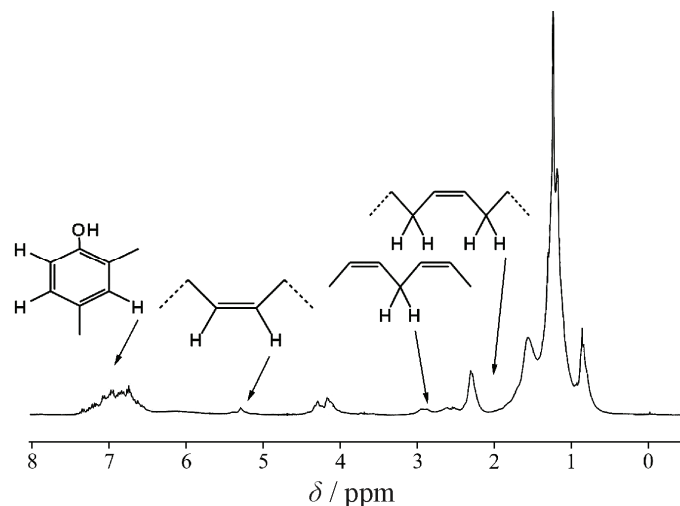


Fig. 3. $^1\text{H-NMR}$ Spectrum of phenolated SBO.

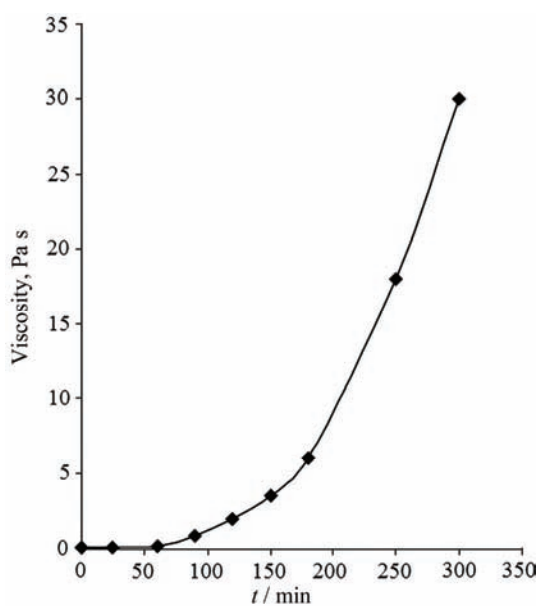


Fig. 4. Variation of the viscosity of the reaction mass during the alkylation reaction of phenol with soybean oil. Catalyst HBF_4 (1 %), $T = 90^\circ\text{C}$.

A gel permeation chromatogram of the product resulting from the phenolation of SBO under conditions of Friedel–Crafts alkylation reactions (catalyst HBF_4 as a 54 % solution in diethyl ether) is shown in Fig. 5. The chromatogram revealed unreacted phenol, phenyl esters of fatty acids, unreacted soybean oil and alkylated phenol products.

The FTIR spectra of phenolated high oleic safflower oil prepared using two catalysts, HBF_4 and triflic acid, together with the FTIR spectra of the initial HOSO

and phenol are displayed in Fig. 6. The double bond content of the phenolated oil (the peak at 3010 cm^{-1}) decreased significantly compared with the initial oil. The formation of phenyl esters as products of side reactions was observed. The peak at 1746 cm^{-1} is characteristic of the carbonyl from the triglyceride ester groups, while the peak at 1719 cm^{-1} is assigned to carbonyl groups from the phenyl esters of fatty acids. Two superacids were used to test their catalytic effect on the phenolation reaction. Triflic acid is stronger than HBF_4 but no significant difference in the phenolation reactions was observed. In earlier experiments, triflic acid gave a slightly more rapid cationic polymerization reaction of oils in the absence of phenols.

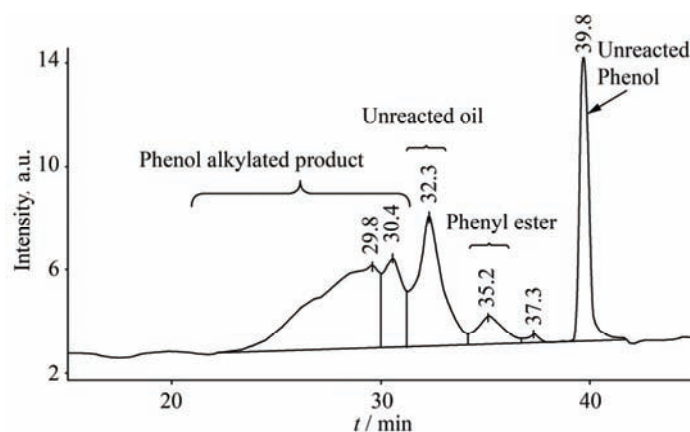


Fig. 5. Typical GPC chromatogram of phenol alkylated with soybean oil.

Phenyl esters were formed to a small extent (less than 10 % in the final phenolated product as measured by the peak area in GPC) by transesterification reactions of triglycerides with phenol, catalyzed by acids (Scheme 3). The position of the peak characteristic of fatty acid phenyl esters was established with a model compound synthesized by transesterification of methyl soyate (methyl esters of soybean fatty acids) with phenol in the presence of a strong transesterification catalyst (stannous octoate), which does not catalyze alkylation or polymerization reactions. It is well known that transesterification of phenols with alkyl esters does not proceed easily, but using an excess of phenol, long reaction time and the continuous removal of methanol resulting from the condensation reaction, it was possible to obtain in a high yield the desired model compound: phenyl ester of soybean fatty acids.

Before running the reaction of phenols with soybean oil, the effect of the catalyst (HBF_4 or triflic acid) on the oil in the absence of phenol was examined under the same experimental conditions. Both superacids polymerized SBO to highly viscous liquids and, at longer reaction times ($>7\text{ h}$), to crosslinked solids.

The cationic polymerization of vegetable oils with superacids is described in detail in a patent.²⁹ The patent showed that the most important fatty acids involved in the cationic polymerization of vegetable oils are the ones with two (linoleic acid) or three (linolenic acid) double bonds and not oleic acid itself. The polymerization of oils differs from the conventional cationic polymerization of olefins since it involves Diels–Alder and “ene” reactions.^{29,30} The structure of polymerized soybean oil presented in Scheme 4 shows that the triglycerides are predominantly linked by cyclic structures as a consequence of Diels–Alder reactions.³⁰

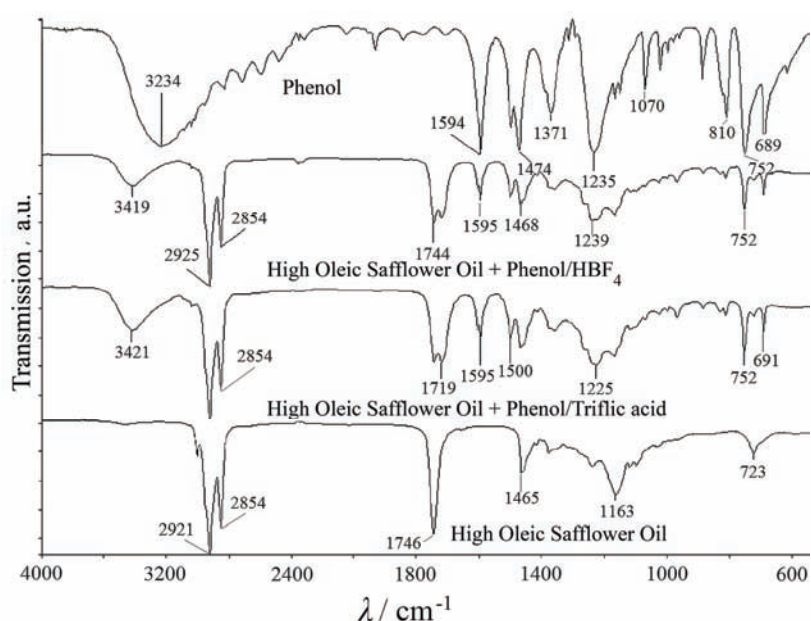
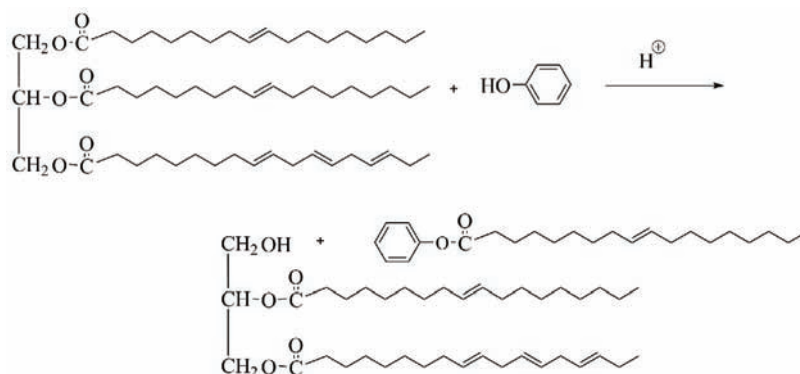
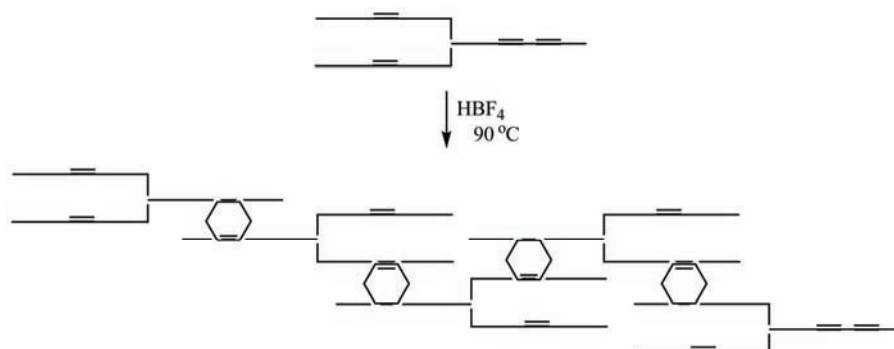


Fig. 6. FTIR Spectra of phenol alkylated with HOSO using HBF_4 and $\text{CF}_3\text{SO}_3\text{H}$ catalysts together with the FTIR spectra of the initial compounds: phenol and HOSO.



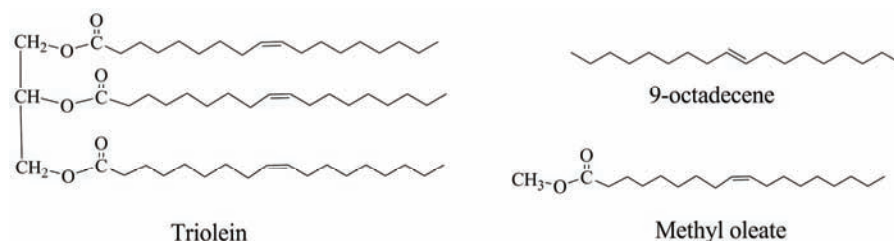
Scheme 3. Formation of phenyl esters by transesterification of triglyceride with phenol.



Scheme 4. Structure of cationically polymerized soybean oil in the absence of phenol. The triglyceride units were linked by the Diels–Alder reaction.

The reaction of oils with phenols results in polymerized phenolated oils because of the simultaneous reactions of cationic polymerization of the oils and the alkylation of phenols with by the oils.

In order to better understand the chemistry, model compounds containing internal double bonds similar to the double bonds in oils were used. The model compounds employed for the alkylation of phenol, presented in Scheme 5, were 9-octadecene, methyl oleate, triolein and HOSO.



Scheme 5. Model compounds containing internal double bonds used to study the Friedel–Crafts alkylation of phenols.

In a similar way, the possibility of the occurrence of cationic polymerization of the compounds with one internal double bond in the presence of superacid catalysts but absence of phenol at the temperature of alkylation was tested. Figure 7 shows only a monomer peak, *i.e.*, 9-octadecene practically does not polymerize in the presence of superacids.

A similar behavior was observed with methyl oleate (Fig. 8), another model compound with only one internal double bond. After 6 h of reaction at 90 °C in the presence of triflic acid, only a very small quantity of dimers of methyl oleate (0.8 %) was obtained.

When triglyceride model compounds with high content of oleic acid (triolein or HOSO) were polymerized under the same reaction conditions, the major com-

ponent after 6 h was the unreacted oil ($\approx 90\%$), accompanied by a small amount of oligomeric oil (less than 10%), as observed in Fig. 9. The composition of this and later mixtures were determined from the GPC peak areas. The reported values are approximate since the detector response factors for each compound are not known.

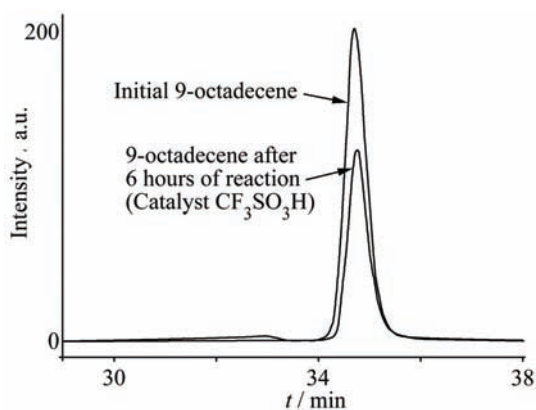


Fig. 7. GPC Chromatogram of 9-octadecene before and after heating for 6 h in the presence of 0.5 % triflic acid.

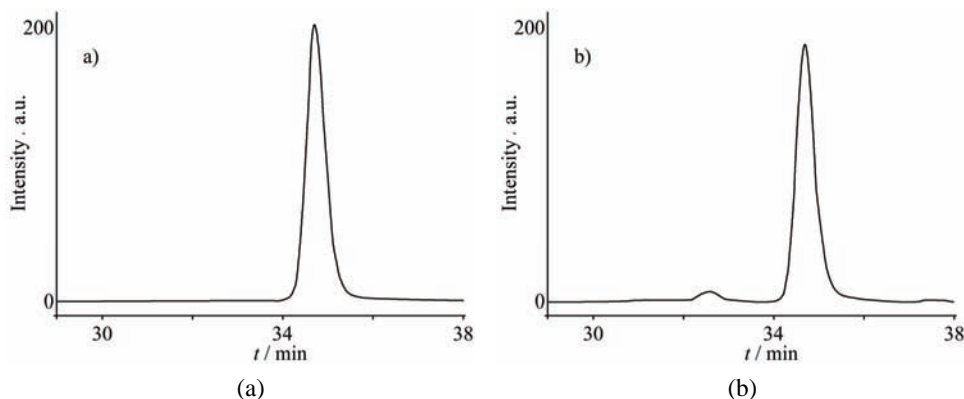


Fig. 8. GPC Chromatogram of a) methyl oleate before and b) after heating of 6h at 90 °C in the presence of HBF_4 as a catalyst.

These experiments led to the conclusion that fatty acids with a single internal double bond do not undergo cationic polymerization. On the contrary, methyl linoleate, having two double bonds, produced 76 % oligomers and polymers and only 24 % unreacted species after 6 h of heating at 90 °C in the presence of triflic acid. The cationic polymerization of soybean oil with superacids under the same reaction conditions produced around 70 % of polymerized oil, due to the high content of fatty acids with two double bonds (linoleic, 52 %) and three double bonds (linolenic acid, 6–9 %).²⁹ Thus, the cationic polymerization of vegetable oils is due to fatty acids with two and three double bonds. On the other hand,

both 9-octadecene and methyl oleate are very reactive in the presence of phenols, leading to very good yields of alkylated phenol products (Figs. 10 and 11).

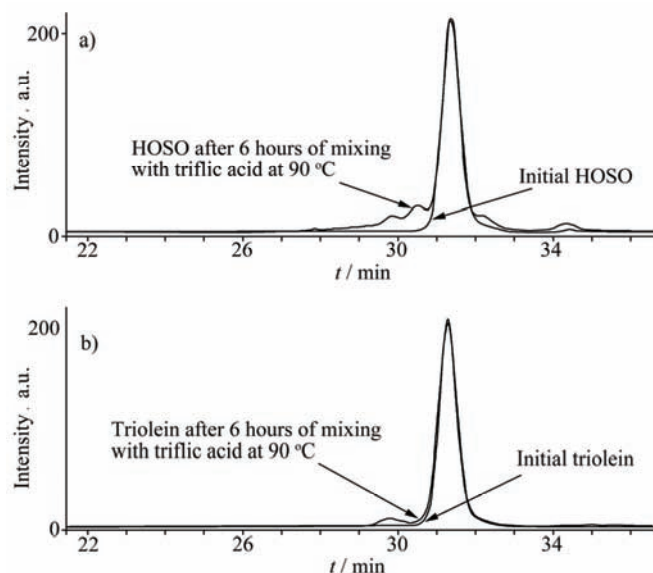


Fig. 9. GPC Chromatogram of a) HOSO and b) triolein before and after mixing for 6 h 90 °C with 1 % triflic acid.

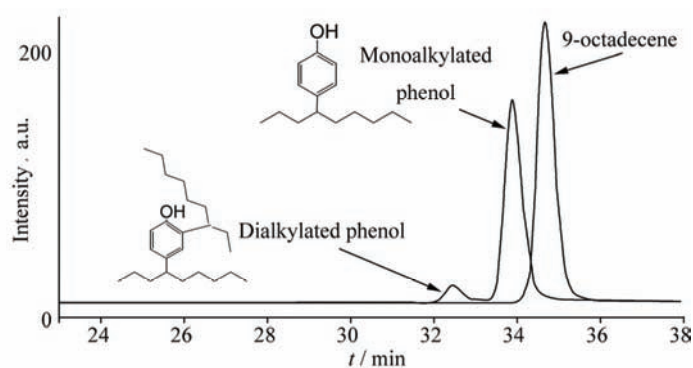


Fig. 10. GPC Chromatogram of 9-octadecene and of alkylated phenol products.

In the case of the phenolation of 9-octadecene, the *IV* decreased from 101 to 10.5 g I₂/100 g, representing a conversion of double bonds of around 90 %. In the case of the phenolation of methyl oleate, the *IV* decreased from 85.7 to 29 g I₂/100g (65 % conversion of the double bonds). The preferred sites for aromatic ring substitution in the Friedel–Crafts alkylation of phenols are the *ortho* and *para* positions (phenol is a trifunctional compound in alkylation reactions having two *ortho* positions and one *para* position available for alkylation). Since the

model compounds with only one internal double bond (9-octadecene, methyl oleate) did not produce oligomers or polymers in the absence of phenol under the same reaction conditions, the only explanation for the formation of oligomers in the alkylation reaction of phenol with 9-octadecene is the Friedel–Crafts mono- and dialkylation of the aromatic ring and mono-, di- and trialkylation in the case of methyl oleate. Both chromatograms presented in Figs. 10 and 11 show the formation of small quantities of di- or even trialkylated products. By analogy, it is possible that during cationic polymerization of oils, di-substitution of the phenolic ring occurs to a small extent, as shown in Scheme 6.

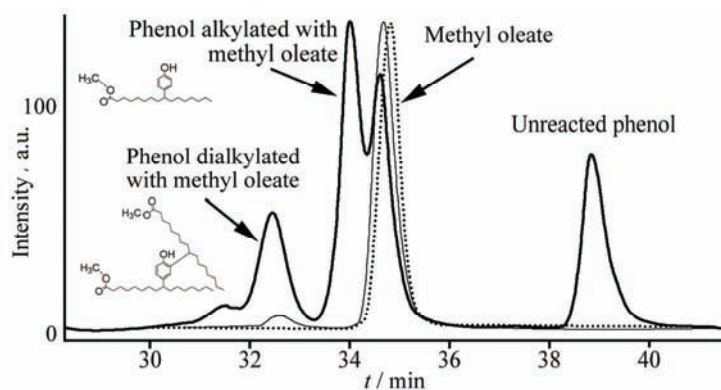
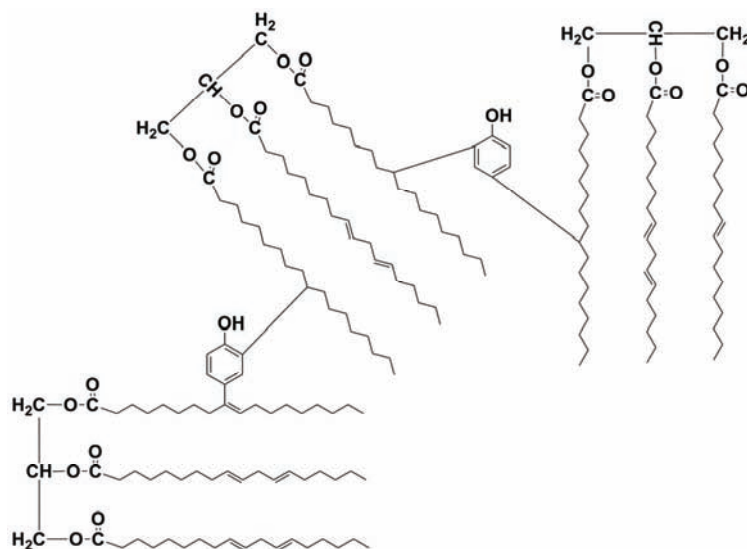
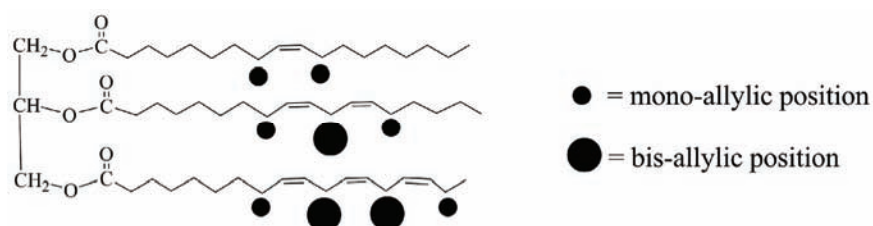


Fig. 11. GPC Chromatograms of methyl oleate, methyl oleate heated with triflic acid (thin line) and phenol alkylated with methyl oleate.



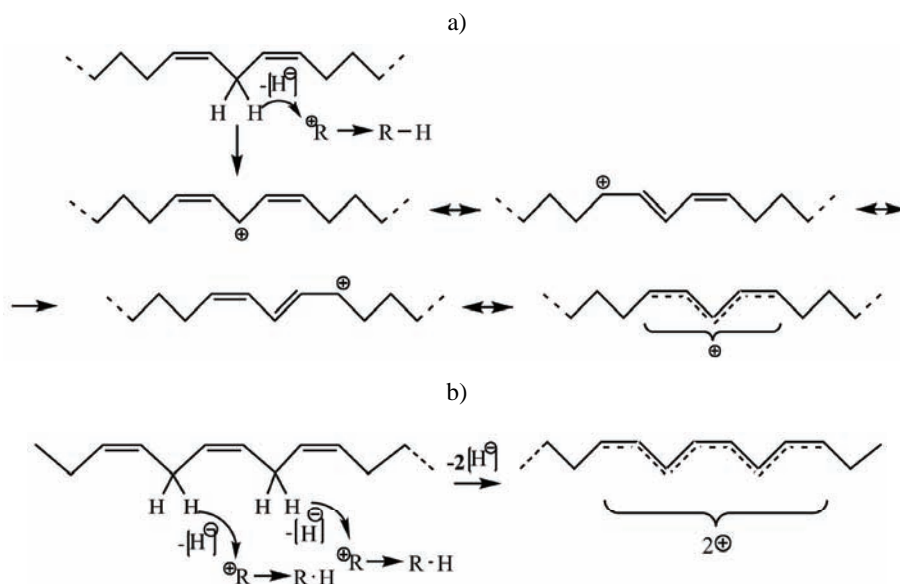
Scheme 6. Formation of vegetable oil oligomers as a consequence of phenol di-alkylation reactions.

Alkylation of phenols with model compounds revealed that the reaction proceeds predominantly with fatty acids having only one internal double bond (oleic acid). Thus, the best oils for Friedel–Crafts alkylation of phenols are those with a high content of oleic acid. The behavior of fatty acids with two or three double bonds under the same reaction conditions is different. Both linoleic and linolenic acids have bis-allylic positions (Scheme 7).



Scheme 7. Mono-allylic and bis-allylic positions in soybean oil.

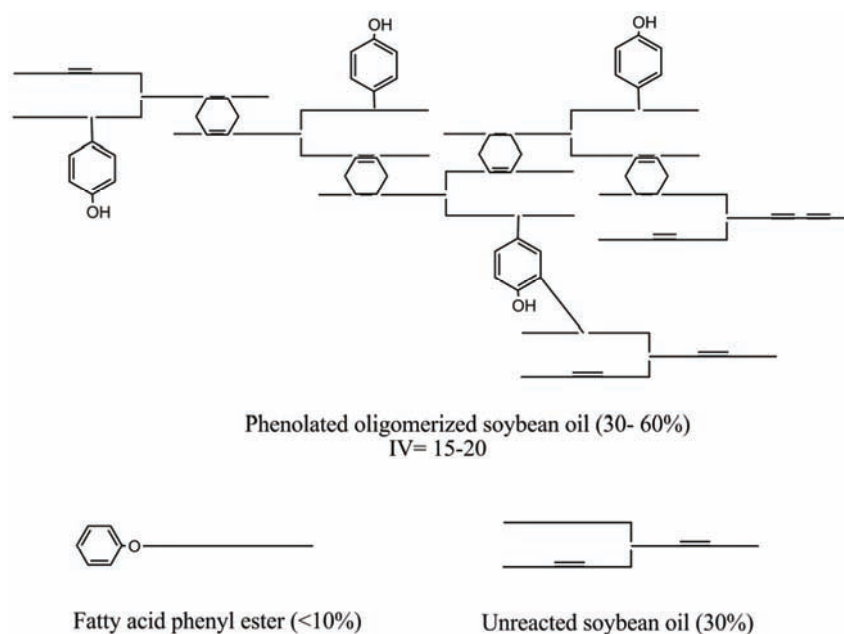
Hydrogen atoms from these bis-allylic positions are easily transferred (as hydride anions) to the carbocations formed by the addition of protons to double bonds (Scheme 2a). As a consequence, very stable allyl cations of low reactivity due to resonance hybrids are formed (Scheme 8). Allyl cations easily form conjugated double bonds which participate in Diels–Alder reactions.



Scheme 8. Formation of stable and low reactivity allyl cations by transfer of bis-allylic hydrogens to carbocations in linoleic and linolenic acids.

Thus, the alkylation of phenols is due to the fatty acids with only one double bond and the polymerization of the oils is due to the fatty acids with two or three internal double bonds and to a small extent due to the phenol di-alkylation reaction.

The most important conclusion of these experiments is that the final product of the Friedel–Crafts alkylation of phenol with the double bonds of vegetable oils is a complex mixture of a polymeric vegetable oil containing phenol units (30–60 %), fatty acid phenyl ester (<10 %) and unreacted vegetable oil (\approx 30 %), as is displayed in Scheme 9.



Scheme 9. Composition of the product resulting from the alkylation of phenol with soybean oil.

CONCLUSIONS

The alkylation of phenols with vegetable oils in the presence of a superacid as a catalyst is a process consisting of two simultaneous reactions: the cationic polymerization of the oils and Friedel–Crafts alkylations.

The product is a complex mixture of alkylated phenol oligomers, fatty acid phenyl esters and unreacted vegetable oil.

The fatty acid structures with one internal double bond (18:1) are more reactive in the alkylation of phenols than the structures with two (18:2) or three (18:3) non-conjugated double bonds. Thus, oils with a high oleic content are much better reagents for phenol alkylation than soybean or linseed oils.

Fatty acids with two non-conjugated double bonds (linoleic) or three non-conjugated double bonds (linolenic) lead preferentially to oligomers and polymers by Diels–Alder reactions and to a lesser extent to alkylated products.

Transfer reactions of carbocations with the bis-allylic hydrogens of 18:2 and 18:3 fatty acids lead to stable and low reactivity allyl cations, inefficient in the alkylation of the phenyl nucleus, but very efficient in the polymerization of oils by Diels–Alder reactions.

The dialkylation reaction of phenols proceeds simultaneously with the cationic polymerization of oils leading to the formation of oligomers and polymers. The phenol rings may link two or more triglyceride units.

Ester bonds are not inert in the presence of phenols, resulting in the formation of phenyl esters to a small extent (<10 %) by transesterification of triglyceride ester bonds with phenols.

The synthesized phenolated vegetable oils are suitable for the preparation of new valuable compounds, such as bio-based aromatic-aliphatic polyols for the synthesis of polyurethanes (by propoxylation, ethoxylation and Mannich reactions); as intermediates for the synthesis of phenol–aldehyde resins with high vegetable oil content, such as bio-based antioxidants, *etc.*

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ИЗВОД

БИЉНА УЉА МОДОФОКОВАНА ФЕНОЛОМ

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У овом раду је приказана синтеза нових биоматеријала модификованих фенолом који су погодни за израду полиуретана. Изучавана је реакција алкиловања фенола различитим уљима биљног порекла у присуству суперкиселина (HBF_4 , “triflic” односно трифлуорометансулфонске киселине) као катализатора. Кинетика реакције је праћена преко смањења садржаја двоструких веза (јодни број) током времена. Да би се боље разумео и објаснио механизам реакције, алкиловање фенола је анализирано коришћењем модел једињења. Као модел једињења са једном унутрашњом двоструком везом су послужили 9-октадецен и метил-олеат, а једињења са три двоструке везе су била три-олеати, као и шафраново уље са великим садржајем олеинске киселине (82 %). Показано је да су масне киселине са само једном двоструком везом као што је олеинска киселина најпогодније за алкиловање фенола. У присуству масних киселина са две двоструке везе (линолна киселина) и три двоструке везе (линолеинска киселина) одиграва се полимеризација уља преко Дилс–Алдерове реакције, што смањује степен одигравања реакције и принос фенил–алкилованих једињења. Производи реакције алкиловања фенола биљним уљима су комплексана смеша фенола алкилованих полимеризованим уљима (30–60 %), фенолних естара насталих трансестерификацијом фенола са триглицеридима (<10 %) и непрореагованих уља (30 %). Фенилована биљна уља могу се посматрати као нове ароматско–алифатске биосировине погодне за израду полиола за поли-

уретане (пропоксиловањем, етоксиловањем, Mannich-овом реакцијом), или као интермедијери у производњи фенолних смола или као антиоксиданси.

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