

Anti-Strip Additive for Bitumen by Processing Lignin

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The study was directed toward modifying of lignin by applying processes of depolymerization alkylation and propoxylation to obtain anti-strip additives for bitumen. Lignin depolymerization was carried out by catalytic hydrotreating on catalyst W-Mo/Al₂O₃ in continuous system and a fixed bed of catalyst. Dispersant characteristics of phenols obtained by lignin depolymerization where improved by increasing the content of hydrophobic groups and of hydrophilic groups, changes made through alkylation and propoxylation of this phenols. Alkylation of cresols was performed in a batch system in the presence of a catalyst phosphotungstic acid supported on mesoporous silica and propoxylation was performed in a batch system in the presence of KOH catalyst. Heterogenous catalysts characterization where performed by determining the acid strength and textural characteristics. The adhesiveness of bitumen is improved by addition of depolymerized-alkylated-propoxylated lignin.

Keywords: lignin depolymerization, heteropoly acids, alkylation, anti-strip additives, bitumen

After cellulose, lignin gains a considerable attention in the last years, representing a major fraction of biomass (10-30%), an abundant, inexpensive and readily available source of renewable materials. Lignin is constituted of polymerised, weakly crosslinked, hydroxyaromatic species and features a high density of benzyl alcohol moieties. Depolymerization of lignin represents a highly challenge for catalytic chemistry due to the complexity structure of lignin through its carbon/hydrogen and carbon/carbon bond types in the monomer units.

The processing of lignin to get valuable chemical products usually consists in several stages. As a first stage in the lignin processing, depolymerization represents a highly challenge for catalytic chemistry due to the complexity structure of lignin through its carbon/hydrogen and carbon/carbon bond types in the monomer units and re-polymerization of the deconstructed polymer. The limitations regarding the depolymerization yield is reported in the literature and yield not exceed 20-23 wt. % of product oil [1]. Literature on lignin depolymerization mentioned different types of lignin depolymerization which might be classified in three main directions, like (i) thermal pyrolysis or thermocatalytical processes, (ii) solvolysis or hydration, (iii) hydroconversion of lignin.

Lignin conversion by thermal pyrolysis or thermo-catalytical processes [2] generally occur in a wide range of temperatures (400-750°C) and the ethers linkages are sensitive at cleavage [3]. Above 400°C, higher yields in liquid products of 40% is obtained, but the tars formation is favored [4]. The catalytic hydro-pyrolysis improves the oil yield. Non-sulfided Ni-Mo/SiO₂-Al₂O₃ and Cr₂O₃/Al₂O₃ catalysts increase the pyrolytic oil yield and modifies the composition of liquid products (methoxyphenols products were replaced by phenol, cresols and xilenols) [5]. The concentration of aromatics (toluene, xylene) increases to roughly 90% in the liquid phase. At 550°C, the yield in liquid phase is only 43 wt% of the initial lignin, while the yield of gaseous phase represented 19 wt% and char/coke 38 wt% coke in the presence of acidic HZSM-5 catalyst using acetone as solvent for lignin [6].

The liquefaction of lignin in the presence of hydrogen-donor solvent improves the yield into liquid products and reduces the coke formation. Tetralin is the most often solvent employed in this process due to its reversible hydrogenation/dehydrogenation ability [2]. The yield into liquid products has low values at 345°C with the formation of condensation products and precursors of coke and chars were formed (20-30%) after C aliphatic-O cleavages. Alternative solvents such as ethanol, glycerol, isopropanol, formic acid or acetic acid were tested to be efficient separately or as mixture [2,7]. Hydrothermal treatments in supercritical conditions at 280-400°C under total pressure of 20-25 MPa preferably in basic media (NaOH 5%) and diluted solutions (10%) lead to phenols compounds such as phenol, catechol and guaiacol, with yield in organic compounds of 20% [8]. In the same time with the lignin depolymerization, the condensation of phenols occurs. Alkali-type catalysts such as K₂CO₃, Ca(OH)₂, Na(OH) have been used in hydrothermal synthesis to avoid the coke formation. The use of mixture of water with other solvents such as water-ethanol, water-formic acid or depolymerization in basic media has been proposed [9-11].

Catalytic hydroconversion of lignin occurs in the presence of bifunctional catalysts (involving both hydrogenation and cracking functions) such as Ni-Mo/Si₂O₃-Al₂O₃ catalyst, either metallic or sulfide form. The obtained conversions have higher values. The phosphorous addition into the catalyst leads to the obtaining of liquid yield (aqueous and organic phase) of 35%. The reaction conditions were temperatures of 350-500°C and pressures of 1-10 MPa [2]. Noble metal-based catalysts such as Ru/C, Pd/C, Rh/C or Pt/C were used under hydrogen pressure with alkanes formation (C₁₄-C₁₈ and C₈-C₉) and methanol [12]. The presence of co-solvent such as dioxane can give the beneficial effects regarding the contact between lignin and catalyst, but the possibility of its degradation or modification in the presence of catalyst should be taken into account. Some authors suggest the utilization of

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obtained compounds from hydro conversion (phenols, cresols) or even the obtained oil from depolymerization of lignin as solvents [2]. The processing of liquefied lignin in order to get liquid fuels has been approached by various catalytic processes. Thus, the reaction rates of deoxygenation and hydrogenation increase by reaching in the temperature from 320 up to 380°C and the obtained products at 380°C are rich in parafines and naftenes. The increasing of temperature favors the increase in the concentrations of cresols and xilenols in aqueous phase. Even if the lignin is the second most abundant natural polymer, no solution for its conversion in liquid fuels was found till now. The depolymerization by cracking or hydrogenolysis and hydro-deoxygenation represents the valuable alternative and wide variety of catalysts for acceleration of process and for increasing of liquid products yield were used.

Hydrodeoxygenation plays a significant role on the upgrading of lignin-derived small molecules which should be performed under mild conditions in aqueous phase over water-tolerant catalysts. HDO can be performed in the presence of various catalytic systems like (i) hydrotreating on Co-Mo and Ni-Mo-based catalysts, (ii) dual functional catalytic systems: Pd, Pt, Ru, Rh on various catalyst supports (C, Al₂O₃, SiO₂).

Conventional hydrotreating catalysts for hydro-deoxygenation are CoMo- and NiMo-based sulfides, industrially used for the removal of sulfur, nitrogen, and oxygen from petrochemical feedstock. These catalysts help for the hydrodeoxygenation upgrading regarding the gas-phase phenol conversion to cyclohexane [13, 14]. The limitation of obtained liquid fuels through hydro-deoxygenation pathway using sulfide catalysts were reported [14, 15] due to the contamination of products via sulfur transfer which require expensive sulfur removal treatment and possible deactivation of the catalysts. The hydro-deoxygenation activity of CoMo sulfide catalysts, non-supported, supported on different supports (alumina, carbon, silica), or modified by K or Pt was studied [16, 17]. The ketonic group is easily and selectively hydrogenated into a methylene group at temperatures higher than 200°C, while a temperature around 300°C is required for the conversion of carboxylic groups as well as for the conversion of the guaiacyl groups [18,19]. Hydro-deoxygenation experiments using CoMoS/Al₂O₃ and NiMoS/Al₂O₃ catalysts were performed by Krause et al. [20-22], suggesting that the activity and stability of CoMoS/Al₂O₃ catalysts for hydro-deoxygenation of phenol and anisole strongly decreased in the presence of H₂S. Subsequently, the formation of coke and high molecular weight compounds on the catalyst surface affected hydro-deoxygenation activity but not the selectivity. It was also found that NiMoS and CoMoS catalysts were much more effective leading to 100% hydrocarbon yield for hydro-deoxygenation of methyl esters compared to their oxide analogs which get 10.5% yield hydrocarbons under identical conditions [21]. In addition, Ni showed higher promoting effect on hydro-deoxygenation activity compared to cobalt in these sulfide catalysts.

Another family catalysts used for optimize the selective hydrodeoxygenation of lignin-derived monomers and dimers to cycloalkanes in the aqueous phase are metal-based catalysts: Pd, Pt, Ru, Rh on different supports (C, Al₂O₃, SiO₂, ASA-amorphous silica alumina containing 20% of alumina) [23-25]. Various reaction temperatures (423, 473, 523 K) and different pH of the aqueous solution (neutral, acidic, basic) were used [25]. The dehydration reaction rate is lower than the hydrogenation reaction and

the keto/enol conversion, requiring a larger concentration of Brønsted acid sites compared to the available metal sites for hydrogenation. Furthermore, guaiacols and syringols aromatic monomers were favorably converted to phenolic compounds with Pd/C catalysts and H₃PO₄. The industrial application of such a process is limited since the added liquid acid (H₃PO₄), leading to a relatively corrosive reaction environment. Advanced hydro-deoxygenation studies [23, 24, 26] combine noble metal Pd with Ni and solid acid Nafion with zeolites. The third generation catalytic systems (Ni on HZSM-5) was reported as active and applicable for hydrodeoxygenation reactions [23].

The objective of this research is to lignin modifying by applying processes of depolymerization alkylation and propoxylation for obtaining anti-strip additives for bitumen.

Experimental part

The raw materials used in experiments were Kraft lignin, tungsten hexachloride, ammonium heptamolybdate tetrahydrate, phosphotungstic acid hydrate, propylene oxide puriss, potassium hydroxide powder, from Sigma-Aldrich, γ -alumina granulated, mesoporous silica MCM-41 and electrolytic hydrogen purity from Linde Company.

Depolymerization of lignin

Lignin depolymerization was achieved by catalytic hydrocracking. The catalyst used 2.6% W - 10% Mo / γ -Al₂O₃ was obtained by successive impregnation with solutions of catalyst precursors, ammonium heptamolybdate and respectively tungsten hexachloride, by pore filling method. Between the steps of impregnating the catalyst was drying at 160°C for 6 hours and calcined at 450°C for 6 h. Activation of the catalyst was carried out by *in situ* reduction in a stream of hydrogen at 5 atm and 450°C for 6 h. Catalyst characterization was performed by determining the acid strength and textural characteristics.

Hydrocracking of the lignin solution (concentration 20%) in water and decalin (mass ratio water / decalin 4/1), with pH 13, was carried out in continuous flow system and a fixed bed of catalyst in a Parr reactor at the following operating conditions:

- temperature: 350°C;
- hydrogen pressure: 70 bar;
- volume hourly space velocities of lignin 0.135 h⁻¹;
- molar ratio hydrogen/ lignin: 60/1.

The reaction products of hydrocracked product after removal of solvents were identified by GC-MS/MS. GC-MS/MS measurements were made by a GC-MS/MS TRIPLE QUAD (Agilent 7890 A) with DB-WAX capillary column (30 m length, 0.25 mm internal diameter, 0.25 μ m film thickness) and helium as carrier gas.

Alkylation of lignin depolymerized

Alkylation of lignin depolymerized was achieved on HPW / MCM-41 catalyst. The catalyst was prepared by impregnating through the pore filling method. The preparation conditions for the catalyst prepared are shown in tables 1.

The catalyst was drying at 160°C for 6 h and calcined at 450°C for 6 h. Catalysts characterization was performed by determining textural characteristics, acid strength distribution and RX spectra. Textural characteristics of the catalysts (surface area, pore volume, average pore diameter, pore-size-distribution) were determined on a Autosorb I Quantacrome. The acid strength distribution of the active center has been determined by the method of thermal desorption of diethyl-amine on a DuPont

Catalyst	Terms of impregnation with HPW			Conc. acid/ acid+ support, wt. %
	Solvent	Support	Conc. acid in solution, g/mL	
30% HPW/ MCM	Ethanol- Water	MCM-41	0.53HPW	30%HPW

Table 1
PREPARATION OF HPW / MCM-41
CATALYST

Catalyst	Specific Surface Area (m ² /g)	Total Pore Volume (cm ³ /g)
W-Mo/ γ -Al ₂ O ₃	204.5	1.297

Table 2
TEXTURAL CHARACTERISTICS OF THE
CATALYST PREPARED

Instruments *Thermal Analyst 2000/2100* coupled with a module *951 Thermogravimetric Analyzer*.

Alkylation process was performed in a batch system, in acid catalysis on a catalyst phosphotungstic acid (HPW) supported on MCM 41. Thus it was used a Berghof autoclave with a 700 mL capacity, disposed with electric heating system in liquid phase reactants dosing and adjustable stirring system, the following values of the operating parameters:

- stirrer speed: 300 rot./min.;
- temperature: 120 °C;
- olefin dosing time: 0.5-1 h;
- molar ratio of 1-octene / phenols: 1.1/1;
- content of the catalyst to the reactants mixture: 1.5%;
- duration of the process: 6 ore.

The reaction products of alkylated product were identified by GC-MS/MS with the same instrument used in the lignin depolymerization step.

Propoxylation of phenols alkylated

Propoxylation of phenols alkylated was performed in a batch system, in a stirred reactor. The process was carried out in liquid phase, in isothermic and isobaric conditions. The process of propoxylation is performed under a nitrogen layer, at the following values of the operating parameters:

- stirrer speed: 300 rpm.;
- temperature: 130°C;
- pressure: 4 atm;
- propylene oxide dosing time: 6 h;
- molar ratio of propylene oxide / phenols alkylated: 8 / 1;
- content of the catalyst to the alkylated phenol: 0.5%;
- duration of the process: 7.5 h.

The catalyst used (potassium hydroxide) is added as an aqueous solution. The reaction product was purified in a continuous reactor type column filled with a cation-exchanger resin (PUROLITE CT 275) for retaining the alkaline metallic ions.

Testing of the additive synthesized

The experimental program of testing the additive synthesized was performed by determining the anti-strip characteristics of road bitumen additivated with 0.5 to 0.8% lignin-based additive. The homogenisation of the bitumen with the additive based on depolymerized lignin was performed in an autoclave equipped with electric heating and stirring, under the following conditions:

- stirrer speed: 300 rpm.;
- temperature: 180°C;
- duration of the process: 6h.

Bitumen additivated was characterized by determining stickiness to the mineral aggregates according to the standard SR 10962 2007.

Results and discussions

Depolymerization of lignin

Textural characteristics of the W-Mo/ γ -Al₂O₃ catalyst determined by BJH method cumulative desorption pore volume, are presented in table 2. The surface area of the catalyst W-Mo/ γ -Al₂O₃ has a typical value for γ -alumina-based catalysts.

Figure 1 shows that the W-Mo/ γ -alumina catalyst possesses a well-defined large pore size with maximum distribution centered around 60Å. This result could indicate that the monomodal pore structure of W-Mo/ γ -alumina catalyst has been induced during γ -alumina preparation.

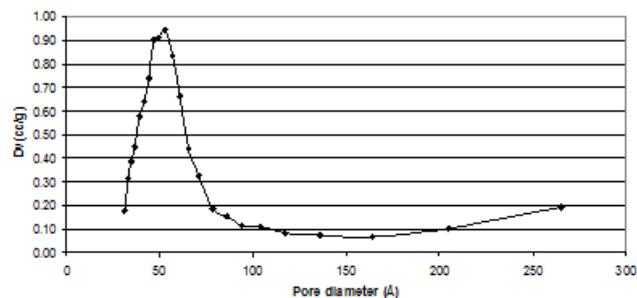


Fig. 1. Pore size distributions of W-Mo/ γ -alumina

Figure 2 shows the thermodesorption of diethyl amine in the temperature range 20-600°C for catalyst W-Mo/ γ -Al₂O₃ (area A - for centers with weak acidity, area B - for centers with medium acidity, area C - for centers with high acidity).

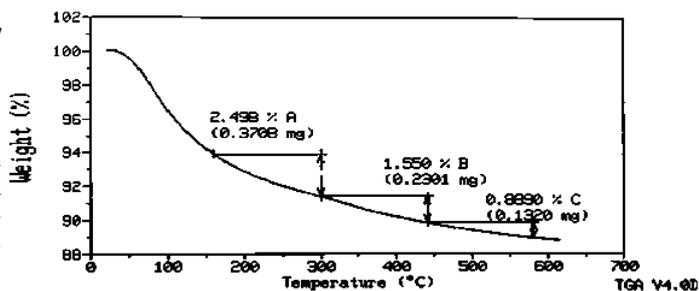


Fig. 2. Thermal desorption curve of diethylamine for the catalyst W-Mo/ γ -Al₂O₃

Table 3 shows the acidity strength distribution for the catalyst W-Mo/ γ -Al₂O₃ determined by thermal desorption of diethylamine curve.

The W-Mo/ γ -Al₂O₃ catalyst contain mostly weakly acidic centers (0.342 meq./g). The concentration of strongly acid centers is lower (0.122 meq./g) and the concentration of medium acid centers (0.212 meq./g) is nearly twice higher than the concentration of strong acidity.

The composition of the final product after removal of the solvent is shown in figure 3. It is noticed that are obtained predominantly phenol and lower alkyl phenols such as cresols or ethyl-phenol but also lower dialkyl phenols.

Table 3
ACIDITY STRENGTH DISTRIBUTION FOR THE CATALYST

The type of the acidic centers	The acid strength, meq./g sample
Weak acids centers	0.342
Medium acids centers	0.212
Strong acids centers	0.122
TOTAL	0.676

41 (area A - for centers with weak acidity, area B - for centers with medium acidity, area C - for centers with high acidity).

On the basis of the thermal desorption curve of diethyl amine was calculated the distribution of the acid strength of HPW/MCM-41 catalyst, presented in table 5. The catalyst contain mostly weak acidic centers (0.521 meq./g). The concentration of strongly acid centers (0.304 meq./g) is slightly lower than the concentration of medium acid centers (0.376 meq./g).

The composition of the final product obtained after alkylation is complex due to the large number of compounds obtained from lignin depolymerization reactions and to the isomerization / cracking of 1-octene which took place in the presence of the alkylation catalyst.

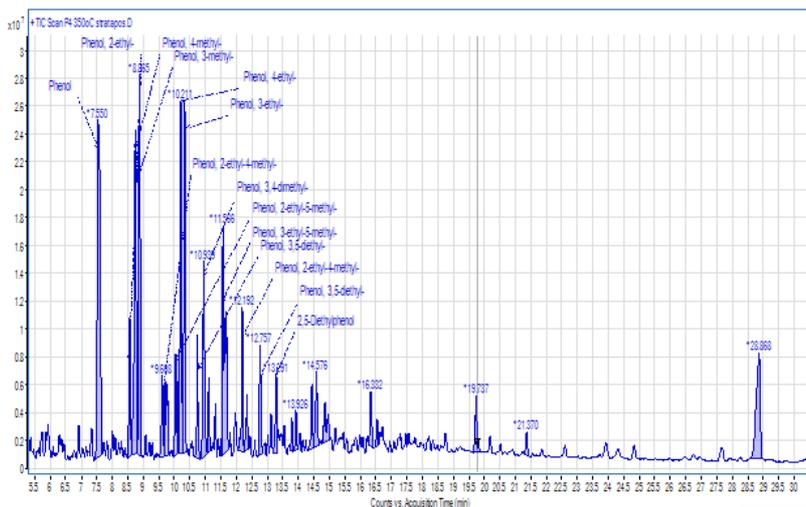


Fig. 3. The composition of depolymerized lignin

Alkylation of lignin depolymerized

Textural characteristics of the support and catalyst used for alkylation of lignin are presented in table 4. The surface area, the pore volume and the average pore diameter changes significantly after the impregnation of the support mesoporous silica MCM-41 with 30% phosphotungstic acid.

RX spectra of MCM-41 support and HPW / MCM-41 catalyst are presented in figure 4.

The formation of hexagonal structure of MCM-41 mesoporous silica is evidenced by a typical low-angle XRD pattern consisting of a strong peak at $2\theta = 2.2^\circ$ along with two small angles at $2\theta = 4.1^\circ$ and 4.4° , respectively.

The XRD pattern of HPW impregnated MCM-41 sample reveals that the peak intensity corresponding to the diffraction from (100) plane is lower as compared to pure MCM-41. The disappearance of diffraction from (110) and (200) planes is an indicative of the loss of long-range ordering of mesoporous structure. Also, the appearance of a large diffraction peak in the range of $2\theta = 5-10^\circ$ could be attributed to the presence of Keggin anions small clusters in HPW/MCM-41 sample.

Figure 5 shows the thermodesorption of diethyl amine in the temperature range 20-600°C for catalyst HPW / MCM-

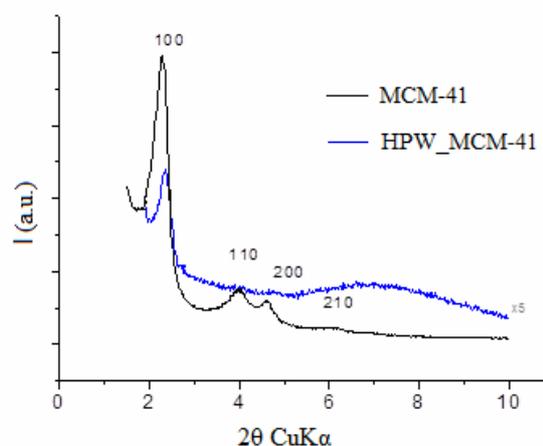


Fig. 4. RX spectra of MCM-41 support and catalyst HPW / MCM-41

It is noticed that are obtained predominantly the alkylation product that contain n-octyl straight-chain alkyl groups, branched alkyl groups such as t-octyl, in the para or ortho position, as well as branched carbon chains smaller such as tert-butyl.

The relatively high acidity of the catalyst and in particular the high content of strong acid centers promoted the

Sample	Concentration HPW on support	Textual Data		
		S _{BET} m ² /g	Pore Volume, cm ³ /g	The average pore diameter, nm
MCM-41 support	-	1230	1.77	26.65
HPW/MCM-41	30%	1414	2.47	18.37

Table 4
TEXTURAL DATA OF THE MCM-41 SUPPORT AND OF THE HPW / MCM-41 CATALYST

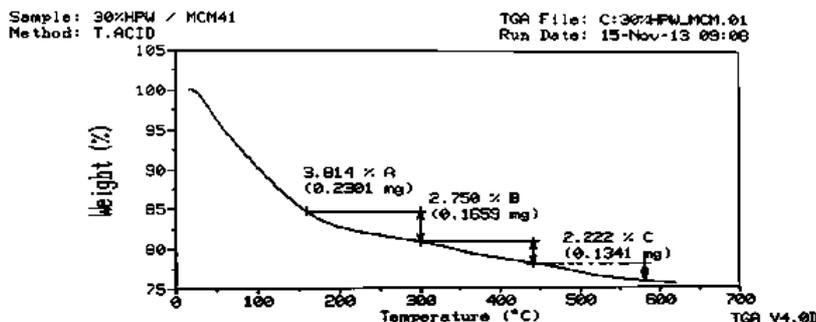


Fig. 5. Thermal desorption curve of diethylamine for HPW/MCM-41 catalyst

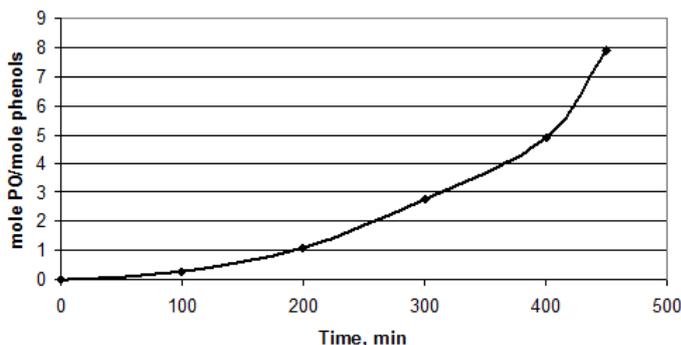


Fig.6. Specific propylene oxide (PO) consumption in time, during alkylated phenols propoxylation (130°C, 4 atm, 0.5%KOH compared to alkylated phenols)

Table 5
ACIDITY STRENGTH DISTRIBUTION FOR
HPW/MCM-41 CATALYST

The type of the acidic centers	The acid strength, meq./g sample
Weak acids centers	0.521
Medium acids centers	0.376
Strong acids centers	0.304
TOTAL	1.201

Bitumen	Natural aggregate	Content of additive, %	Adhesiveness, %
D 70/100	Chileni Sort 5-8	0	93.53
		0.5	95.04
		0.8	95.83

Table 6
INFLUENCE OF THE ADDITIVE BASED
DEPOLYMERIZED LIGNIN ON
BITUMEN ADHESIVENESS

reaction of 1-octene cracking to lower alkenes such as tert-butenes, while the high content of the medium strength acid centers promoted the isomerization reaction of 1-octene to branched product such as tert-octenes.

Propoxylation of alkylated phenols

Figure 6 represents the specific consumption of propylene oxide in time during propoxylation of alkylated phenols. As can be observed from figure 6, the reaction present an induction period when the process follow with low rate, behaviour probable due to relative high acidity of phenols.

Increasing the propoxylation degree leads to diminishing of phenols acidity, which favors an accentuation of reaction speed. Thus, for a reaction time more than 400 min., the propoxylation reaction rate increases rapidly.

The termination of alkoxylation process is evidenced by decreasing the pressure on the system and epoxide conversion is complete. The reaction product was purified in a column reactor in order to remove alkali metal ions, a process which was performed by ion exchange on a strongly acidic cation exchange resin. The characteristics of surfactant obtained are:

- appearance: viscous liquid pale yellow- light brown color;
- pH 1% aqueous solution: 6.8;
- hydroxyl value: 72 mg KOH/g;
- alkalinity (expressed as content in KOH): <0.01%gr.;
- density: 0.97 g/cm³;
- water content: 0.13%.

Testing of the additive synthesized

The efficiency of synthesized additive was evaluated by addition of this additive to bitumen D 70/100 at 0.5 and 0.8% concentrations. Homogenization of the bitumen additivated was carried out by mechanical stirring using an stirrer anchor-type at 160°C for 6 h. Adhesiveness of road bitumen 70/100 in the presence of the additive synthesized on natural aggregates Chileni with 5-8 mm size is presented in table 6.

It can be observed an increase of the bitumen adhesiveness compared to the standard mineral aggregates of 5-8 mm size with increasing additive ratio, the increase being more pronounced at lower additive concentrations (1.6 for 0.5% concentration and 2.4 for 0.8% concentration).

Conclusions

The hydrocracking process of lignin with W-Mo / γ -Al₂O₃ catalyst favors the obtaining of phenol and lower alkyl phenols such as methyl-phenols.

Alkylation of depolymerized lignin on HPW / MCM-41 catalyst favored obtaining of alkylation product that contain linear alkyl groups like n-octyl, branched alkyl groups such as t-octyl in para or ortho position and lower branched chains such as tert-butyl.

The high concentration of stronger acidic centers of the catalyst HPW / MCM-41 probably favored obtaining of alkyl-phenols with smaller side chain such as tert-butenes, while the high content of the medium strength acid centers favor the obtaining of alkyl-phenols with branched chains such as tert-octenes.

The propoxylation of alkylated phenols present an induction period when the process follow with low rate, behaviour probable due to relative high acidity of phenols. Increasing of the propoxylation degree lead to diminishing of acidity phenols, that favors an accentuation of reaction speed.

Additivating of bitumen D 70/100 with propoxylated-alkylated-phenols at concentrations of 0.5% and 0.8%, favored the increase of bitumen adhesiveness on these mineral aggregates.

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