COMPARATIVE KINETIC ANALYSIS OF POPLAR BIOMASS ALKALINE HYDROLYSIS

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Lignin-based low-molecular phenol compounds produced by alkaline hydrolysis of vegetable biomass – poplar wood and poplar bark – can be used to increase the chemical stability of automobile petrol fuels. The comparative kinetic analysis of alkaline hydrolysis of both types of poplar biomass outlines the effect of the process duration and NaOH concentration on the toluene extract production in the course of the alkaline hydrolysis. The applicability of different kinetic equations describing the process kinetics is verified. The values of the initial and the current rate are calculated. The amount of low-molecular phenol compounds obtained from poplar bark biomass is higher and the relative decrease of the current rate in the course of the process is smaller in spite of the higher lignin content. A kinetic equation, valid for both types of poplar biomass, connecting the desired extent of hydrolysis with the variables of the process is suggested.

Keywords: kinetic analysis, poplar biomass, alkaline treatment, phenol compounds

INTRODUCTION

Lignin is a wide spread, renewable, amorphous natural polymer, containing phenylpropane units. The latter are derivatives of syringol, guaiacol and p-hydroxyphenol. They are interconnected through ether and C-C bonds, thus forming a very complex three-dimensional polymer matrix.[1-2] They are in fact the source of low-molecular phenolic compounds (LMPC).[3-7] The alkaline hydrolysis of lignin results in its depolymerization through the rupture of ether and cleavage of C-C bonds connecting the phenylpropane units. The method leads to the production of low-molecular monomer phenols (2,6-dimethoxyphenol; 3,6-dimethoxy-4-hydroxy acetophenone; 4-ethylguaiacol; 2-methoxyphenol; 4-ethyl-2-methoxyphenol; 2-methoxy-4-propylphenol; 4-methylcatehole; phenol; 4-hydroxy-3,5di-methoxyben-zaldehyde and 4-hydroxy-3-methoxy-benzaldehyde, whose separation and chromatographic identification is comparatively easy.[8-11]

Nenkova *et al.*[4-6] studied the alkaline hydrolysis of technical hydrolysis lignin and other biomasses (poplar wood and poplar bark) under different conditions (temperature of 180 °C, duration of 2, 4 and 6 h, 3, 5 and 7% aqueous solution of NaOH, lignin/aqueous solution of NaOH ratio (hydromodule) of 1:6, 1:8 and 1:10). The nature and the possible application of the low-molecular products, which are left in the liquid phase after the precipitation of the higher-molecular fraction was investigated. These compounds can eventually be used as antioxidation additives to petroleum fuels.[12-13]

Considering this, the objective of the present work has been to make a comparative kinetic analysis of the alkaline hydrolysis of poplar wood and poplar bark biomasses for production of low-molecular phenol compounds.

EXPERIMENTAL

The chemical composition of poplar wood sawdust and poplar wood bark was determined according to R. Draganova[14] and is shown in Table 1.

The alkaline hydrolysis of poplar wood bark was carried out in rotating steel autoclaves, heated in a bath of polyethyleneglycol, at the temperature of 180 °C, for 2, 4 and 6 hours. An aqueous solution of NaOH (3, 5 and 7 % by weight) was used as a depolymerization agent, at different lignin:NaOH water solution ratios (hydromodule) – 1:6, 1:8 and 1:10. The treatment of the poplar wood sawdust was performed under the same conditions, where anthraquinone was added as a

catalyst (0.5 wt%). Anthraquinone is a delignifying agent, widely utilized in the production of technical cellulose for preserving the carbohydrate part.[15] The degraded lignin suspension obtained by alkaline treatments was filtered and the quantity of undissolved lignin was determined. The high molecular mass lignin fraction was precipitated by acidification of the liquid phase with HCl (2 mol/L) to pH ~1-2. The volume of the liquid part separated by filtration, under vacuum, was reduced on a rotary evaporator. A triple extraction was carried out for toluene, at a constant water phase ratio of 1:5. The toluene extract was dried up with anhydrous Na_2SO_4 and then filtered. The procedure of separating and extracting reaction products is shown in Figure 1.

The low-molecular compounds were identified by GC-MS analysis on a Hewlett-Packard gas chromatography unit, model 6890, equipped with a mass selective detector, model 5973. A 30 m x 0.25 mm I.D. capillary column HP 5 with a film thickness of 0.25 μm was used. The splitless injector was maintained at 280 °C. High-purity helium was employed as a carrier gas, at a constant flow rate of 0.8 mL/min[-1]. The initial column temperature was set to 80 °C and maintained for 1 min. Then, the following temperature program was applied: heating to 190 °C at a heating rate of 15 °C/min, heating again at 5 °C/min to 280 °C, maintaining for 10 min and then cooling to 80 °C. The mass of the extracted products was determined after removing the solvent on a rotary vacuum vaporizer.

RESULTS AND DISCUSSION

The influence of NaOH concentration and process duration on the dissolved lignin yield and the yield of obtained low molecular phenolic compounds (LMPC) was studied. The results are shown in Table 2.
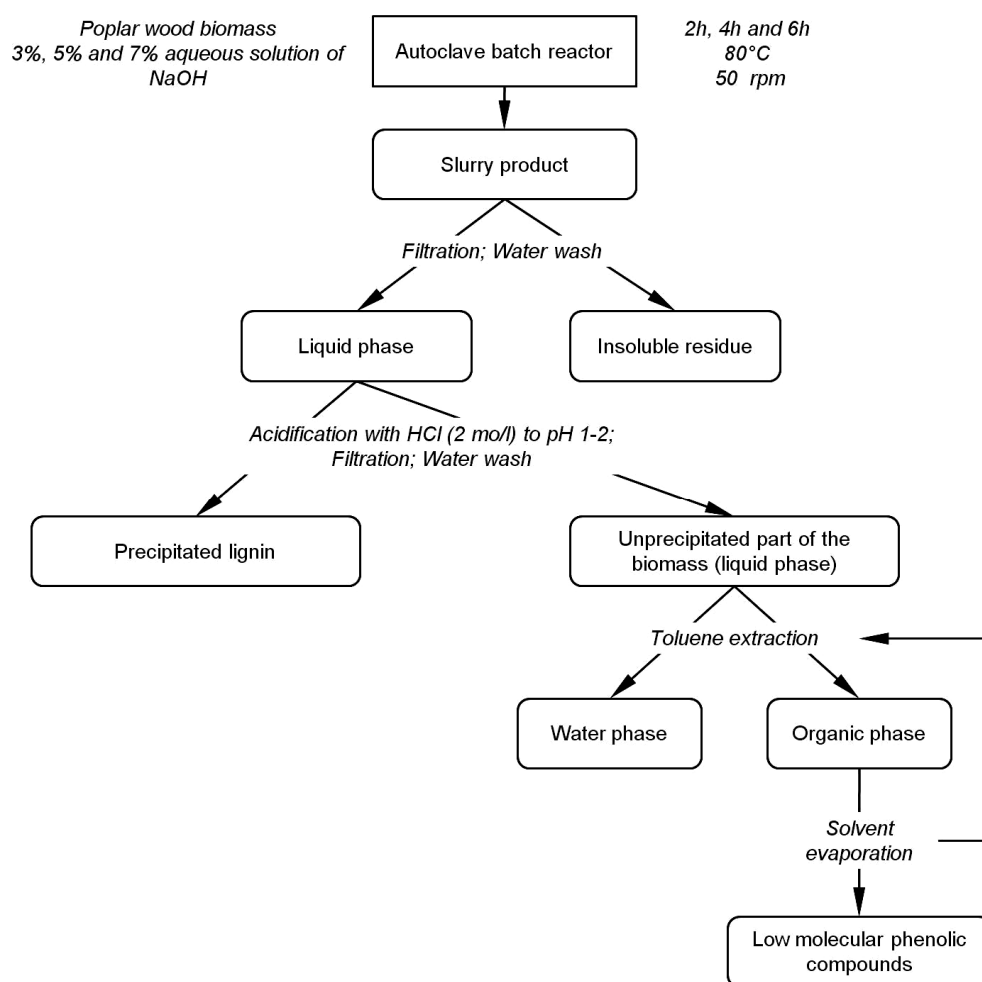

Figure 1: Scheme of low-molecular phenolic compounds production

Table 1
Chemical composition of poplar wood bark and sawdust

Material	Amount (%)		
	Pentosans	Cellulose	Lignin
Poplar wood bark	20.10	35.80	37.22
Poplar wood sawdust	18.50	43.85	25.20

Table 2
Amount of dissolved lignin and obtained toluene extract versus concentration of NaOH (c_0, %)
and process duration (h)

Duration (h)	Dissolved part of lignin (%$_{of\ initial\ material}$)						Toluene extract (%$_{of\ initial\ material}$)					
	Sawdust			Bark			Sawdust			Bark		
	Concentration of NaOH, c_0 (%)											
	3%	5%	7%	3%	5%	7%	3%	5%	7%	3%	5%	7%
2	25.83	55.85	60.59	44.22	69.09	72.97	0.76	1.58	2.19	0.44	0.91	1.26
4	29.76	58.50	63.88	46.88	71.02	75.95	1.07	1.94	2.52	0.67	1.40	1.82
6	30.90	58.36	64.23	47.40	71.35	76.35	1.23	2.24	2.91	0.71	1.48	2.05

Table 3
Relative increase of toluene extract quantity, α, for different types of biomass as a function of
process duration and NaOH concentration

Duration (h)	α					
	Sawdust			Bark		
	NaOH concentration					
	c_0=3%	c_0=5%	c_0=7%	c_0=3%	c_0=5%	c_0=7%
0	0.00	0.00	0.00	0.00	0.00	0.00
2	0.26	0.54	0.75	0.21	0.44	0.61
4	0.36	0.66	0.86	0.33	0.68	0.89
6	0.42	0.77	1.00	0.35	0.72	1.00

The results show that with an increase of NaOH concentration from 3 to 5%, the destruction of the biomass components is considerably extended (Table 2). Respectively, the quantity of the produced low-molecular phenol compounds increases twofold. Although to a smaller degree, this trend is maintained with the subsequent increase of NaOH concentration to 7%. An extension of the process duration, while maintaining the other conditions similar, also favors the increase of low-molecular phenol compounds quantity. The highest production of low-molecular phenol compounds was obtained when treating the biomass by 7% NaOH for 6 h, at the temperature of 180 °C and hydromodule of 1:8. For the poplar wood, the maximum production was recorded as T_{max}=2.91%, and for the barks, as T_{max}=2.05%.

The dimensionless quantity α is introduced as a kinetic variable, aiming to compare the kinetic characteristics of the process investigated. It is defined by:

$$\alpha = \frac{T}{T_{max}} \qquad (1)$$

where T is the quantity of the toluene extract at a given moment of the process, while T_{max} is its maximum amount for the respective raw material used.

The kinetic variable α stands for the current extent of the alkaline hydrolysis process or the relative growth of the quantity of the toluene extract containing low molecular lignin products. The values of α as a function of the alkali quantity used and time are presented in Table 3.

The kinetic curves α vs. t referring to poplar wood sawdust and poplar bark are presented in Figure 2. Fig. 2 shows that the process for both raw materials is favored by a NaOH concentration increase. The latter is better outlined in the range from 3% to 5% than in that from 5% to 7%. It is evident as well that the values of α are higher for the wood sawdust than for the bark.

The applicability of different kinetic equations describing the kinetics of heterogeneous processes (Table 4) has been verified. It was found that the best description of the process studied is provided by the exponential kinetic equation valid for processes taking place on uniformly inhomogeneous surfaces.

The latter equation[16-18] is given by:

$$v = v_0 e^{-a\alpha} \qquad (2)$$

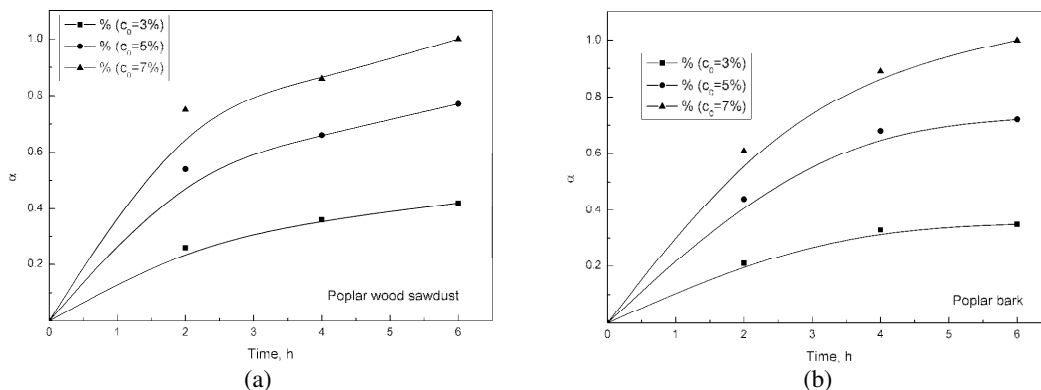where $v = d\alpha / dt$ and v_0 are the current and initial rate of alkaline hydrolysis, respectively.

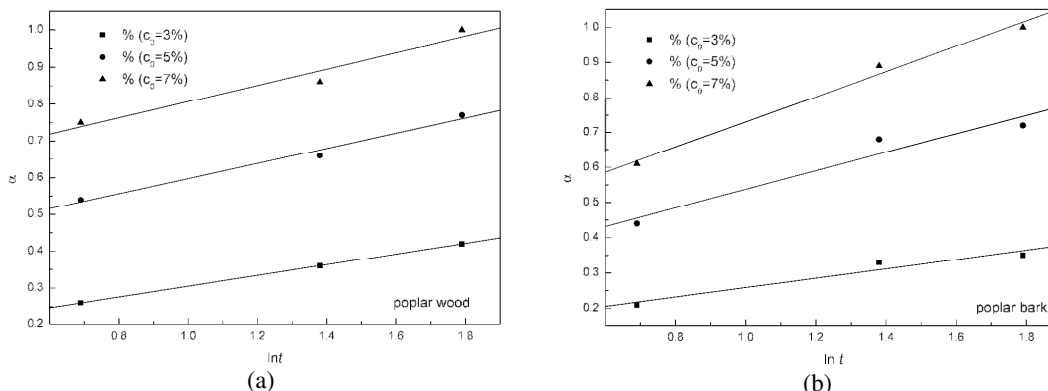Figure 2: Kinetic curves α vs. t for poplar wood sawdust (a) and poplar bark (b)

Figure 3: Linearization of kinetic curves in coordinates α vs. ln t for poplar wood

Table 4
Kinetic equations describing the kinetics of heterogeneous processes

Equation	Correlation coefficient R					
	Poplar wood sawdust			Poplar wood bark		
	3%	5%	7%	3%	5%	7%
First order equation $\ln Pc = const - kt$	0.960	0.954	0.987	0.910	0.900	0.950
Exponential equation $Pc = A + B \ln t$	0.999	0.992	0.988	0.971	0.971	0.995
Power equation $\ln(Pc) = \ln g + \chi \ln t$	0.998	0.998	0.981	0.964	0.960	0.990
Topochemical equation $\ln(-\ln(Pc)) = n \ln k + n \ln t$	0.999	0.984	-	0.971	0.973	-

According to the model of uniformly inhomogeneous surfaces, the active centers on the biomass surface are linearly distributed depending on their energy and entropy. For that type of surfaces, the rate of the heterogeneous reactions decreases exponentially with an increase in the extent of the reaction, α.

The heterogeneity kinetic coefficient a takes into account the energy and entropy inhomogeneity of the system.

All kinetic curves are linearized in coordinates α vs. ln t corresponding to the approximated integral form (3) of the exponential kinetic equation (Eq. 2):

$$\alpha = \frac{1}{a}\ln\left(v_0 a\right) + \frac{1}{a}\ln t \tag{3}$$

Fig. 3 presents the linear dependences obtained for the poplar wood; a similar tendency has been observed for the poplar bark.

Table 5
Values of heterogeneity kinetic coefficient, a, and the initial process rate v_0 (h^{-1}) for different concentrations of NaOH

c_0 NaOH (%)	Poplar wood		Bark	
	a	v_0 (h^{-1})	a	v_0 (h^{-1})
3	6.6	0.27	7.6	0.28
5	5.0	0.52	3.8	0.61
7	4.5	0.82	2.8	1.08

Table 6
Values of the apparent rate constant k and coefficient b

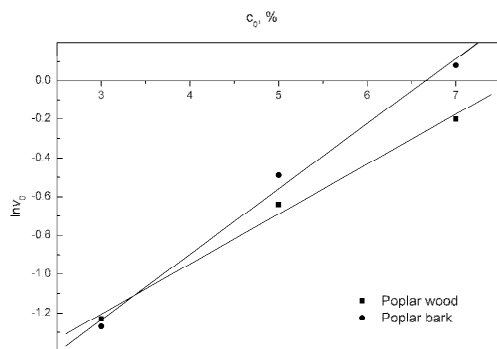| Material	b	k (h^{-1})
Poplar wood sawdust	0.25	0.138
Poplar wood bark	0.33	0.105

Figure 4: Linearized dependence of the initial rate (ln v_0) on NaOH concentration (c_0) for both types of poplar biomass
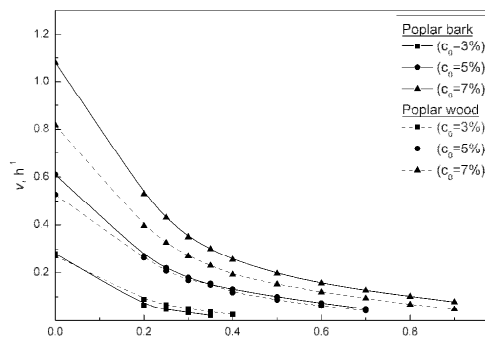

Figure 5: Process rate v (h^{-1}) versus the extent of conversion for poplar wood and poplar bark

The heterogeneity kinetic coefficient *a* (Eq. 3) is calculated based on the slope of the straight lines presented (Figure 3). Table 5 summarizes the values obtained. The heterogeneity coefficient decreases with a NaOH concentration increase. This tendency is better outlined for the bark investigated.

The values of the initial process rate v_0 (h^{-1}) are calculated according to Eq. (3), and are presented in Table 5. It may be noted that the initial rate in the case of bark hydrolysis is higher than that for wood sawdust. Besides, the increase in NaOH concentration affects more favorably this hydrolysis process. It is probably due to the higher initial lignin content in this type of poplar biomass. Table 5 also shows that the initial rate increases with a NaOH concentration increase. The dependence of v_0 on the amount of the base used can be described by the following equation:

$$v_0 = ke^{bc_0} \tag{4}$$

where b is a coefficient that does not depend on NaOH concentration, while k stands for the apparent rate constant of the process. The equation obtained is valid for both types of poplar biomass. The linearized form of Eq. (4) is illustrated in Fig. 4. The calculated values of coefficient b and of the apparent rate constant k (h^{-1}) are presented in Table 6. The current rate of

enzyme hydrolysis v (h^{-1}) for different values of α is calculated based on Eq. (2). The dependences obtained are illustrated in Fig. 5. It is seen that the current rate increases with the increase of NaOH concentration and decreases in the course of the process for both types of biomasses.

Figure 5 shows that the hydrolysis runs faster for poplar bark than for poplar wood at the start of the process. The rate for the wood becomes commensurate with that for the bark at α greater than 0.25 in spite of the lower initial lignin content in this biomass. The relative decrease of the current rate in the course of the process for poplar wood is smaller. In the case of wood hydrolysis, the greater part of the lignin contained dissolves and the production of low-molecular phenol compounds is higher than that for the bark. This is probably due to the added anthraquinone, which acts as a catalyst. It not only helps protect the polysaccharides against destruction, but also facilitates the destruction of the lignin macromolecule to low molecular phenol compounds. On the other hand, the lignin in the bark is more concentrated than in the wood, but the access to it is hampered. In the course of the process for the raw materials studied, the rate decreases because of the exhaustion of the active centers on the lignin surface.

The juxtaposition of Eq. (4) and Eq. (3) leads to the following relation between the extent of hydrolysis, α, the time t and NaOH concentration, c_0:

$$\alpha = \frac{1}{a}\ln\left(akt\right) + \frac{b}{a}c_0 \qquad (5)$$

Equation (5) presents the general dependence of the extent of the process, α, on the variables t and c_0. The constants a, b and k are characteristic of the process studied. This expression is of practical importance too because it can predict the desired value of α by choosing in advance the time for treating the biomass, as well as the concentration of NaOH required. For example, Eq. (5) gives $\alpha=0.88$ in the case of poplar bark providing $c_0=7\%$, t=4 h, a=2.8, b=0.33 and k =0.105 h^{-1}. In case of poplar wood, Eq. (5) gives $\alpha=0.31$ if $c_0=3\%$, t=4 h, a=6.6, b=0.25 and k=0.138 h^{-1}. These values of α are in good agreement with the experimental one.

CONCLUSION

A comparative kinetic study of the alkaline hydrolysis of poplar wood sawdust and poplar bark is carried out. The process kinetics is described by an exponential kinetic equation. Its application provides the determination of the initial and the current rate of the process. In spite of the higher lignin content of the initial poplar bark biomass, the amount of the toluene extract is higher and the decrease of the process current rate is lower that that in case of poplar wood sawdust. A kinetic equation valid for both types of poplar biomass is suggested. It connects the extent of hydrolysis which is aimed with the time and base concentration provided.

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