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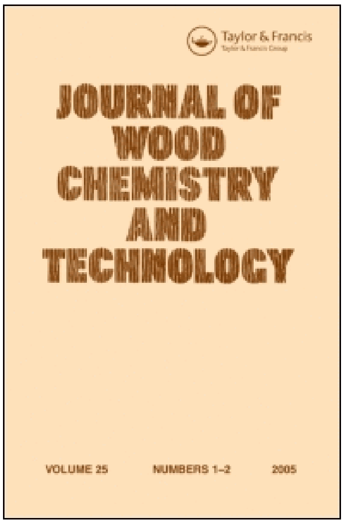

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HYDROLYTIC DEPOLYMERIZATION OF A STEAM EXPLOSION LIGNIN

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ABSTRACT

Alkaline hydrolysis of a hardwood lignin (Populus tremuloides) obtained from a steam-aqueous treatment has been studied experimentally. It was found that the main degradation products were catechols, syringols and guaiacols. In the study, the effects of the reaction conditions, such as temperature, reaction time, alkali concentration as well as the lignin origins on the yields of the monomers produced, have been exploited. Under the drastic conditions (350°C for 10 min), about 9% (w/w of initial lignin) catechols could be obtained. At low reaction severity, however, syringol and guaiacol were the predominant products. Alkali concentration also influenced obviously the degradation and demethylation of the lignin and its derivatives.

Key words: lignin, steam explosion process, alkaline hydrolysis, catechol, guaiacol, syringol.

INTRODUCTION

Lignin constitutes 20-35% of hardwood and 15-25% of softwood depending on the tree species. It is a three-dimensional, thermoplastic, amorphous polymer derived from copolymerization of three phenylpropanoid (coumaryl, coniferyl and

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sinapyl) alcohols. These structures are linked by a multitude of interunit bonds that include several types of ether (ß-0-4, α-0-4 and 4-0-5) and carbon-carbon linkages.

In order for lignin to be utilized as a raw material, it first has to be isolated from other wood components. Presently, isolation of lignin mainly occurs in chemical pulping, including organosolv, sulphite and Kraft processes. In these processes, lignin is modified chemically due to depolymerization and recondensation, the focus being to recover the cellulose, not the lignin. The modification provides a lignin that has some uses in further reactions. Since the beginning of the 80's, some studies at the University of Sherbrooke (Quebec, Canada)[1,2] have been focused on a method of isolating lignin from wood using a steam explosion technique. Compared to other processes, the steam-aqueous treatment is more effective as a process to isolate lignin from other wood components. Its advantages are simplicity; the limited number of extractive steps; and less modification on lignin structures.

Many uses of the isolated lignin have been suggested and tested for several decades. Currently, its use predominately as fuel results from the fact that in the Kraft process, spent liquor incineration is used for the recovery of process chemicals and its energy. The decision to investigate lignins possibilities is based on the fact that lignin may be used as polymers, such as adhesive for board manufacture and dispersants used in oil fields, or be degraded into such low molecular weight chemicals as aromatic monomers. The utilization of the isolated lignins as polymers will be enhanced if they can be distinguished from other components, such as sugar and its derivatives, coming from the isolation processes in terms of chemical structures, mechanical properties, and product performance characteristics. In the latter case, (because of its complex structure) conversions of lignin by degradation most often result in a multitude of products. The problem of separating such a mixture into marketable components has probably been the major impediment to exploiting lignin as a source of chemicals[3]. To resolve this problem, an increase of reaction selectivity in the conversion of lignin into similar products is necessary. These processes will simplify the product mixture, avoid some of the separation problems, and give increased yields of marketable products[4].

Among the degradation reactions of lignin into monomers, hydrolysis in basic media has received attention due to the rather few simple degradation products obtained. Clark and Green[5] studied the production of phenols from alkaline hydrolysis of Kraft lignin and found that catechol was the most abundant monomeric product that represented 5.3% of the lignin at the optimum conditions. Thring *et al.*[6] isolated lignin from *Populus deltoides* using ethylene glycol as solvent and depolymerized this lignin by alkaline hydrolysis. About 11% total phenols and 9% Catechols (based on the initial lignin) were obtained at the optimum conditions. The other advantage of this method is that the catalytic reagent (NaOH) is inexpensive and available commercially and requires no elaborate method of preparation.

The goals of the investigation were three-fold: (a) to produce a lignin in the steam explosion process from a hardwood (*Populus tremuloides*); (b) to obtain monomeric phenol products, mainly catechols, syringols and guaiacols, from this lignin by alkaline hydrolysis; and (c) to exploit the effects of reaction conditions and the lignin origins.

MATERIALS AND METHODS

Wood material

The wood material used for this study was derived from *Populus tremuloides* grown in the Eastern Townships, Québec (Canada). They were debarked and chipped. The compositions of this wood material were determined by using the standard methods (ASTMD-1107 for alcohol-benzene extractive; ASTMD-1787 for pentosans; ASTMD-1103-60 for α-cellulose; ASTMD-1106 for Klason lignin and ASTMD-1102 for ash). They are (in % wt m.a.f. wood):

Ethanol-toluene extractive	:	3.6%
Pentosans	:	19.0%
Cellulose	:	51.6%
Klason lignin	:	20.6%
Ash	:	0.4%

The balance to 100% is made of acid-soluble lignin and hexoses present in the hemicelluloses. The chips were used at moisture contents between 45 and 55% of the total weight of the chips.

Production of the steam explosion lignin

The hardwood fractionation was conducted in a 4 tonnes/hr pilot plant STAKE II located at the University of Sherbrooke (Quebec). This technique has been described elsewhere[2]. The aim of the steam-aqueous treatment here was to produce lignin. The treatment (220°C, 2 min) was followed by three steps (see Figure 1):

[1] hot water extraction of the treated chips to recover the soluble sugars (T: 70°C, t: 30 min);
[2] an alkaline delignification of the treated chips (T: 100°C, t: 30 min);
[3] the precipitation and the recovery of the lignin with H_2SO_4 (T: 80°C, t: 10 min, pH = 1.8).

The lignin obtained was labelled LVH, which represented 70% of the Klason lignin in the original material. Analysis of the C.H.N. contents (C: 64.0%, H: 6.5%, N: 0.15%) of the lignin clearly indicated that the alkaline extracted lignin has a similar component to the corresponding Klason lignin.

Depolymerization of lignin

Alkaline hydrolysis of lignin was conducted in a 500 ml magnetically stirred autoclave. In typical experiments, 5 g lignin, 98 g water and 2 g NaOH, corresponding to 2% alkali concentration, were placed in the autoclave. The autoclave was sealed. After purging with nitrogen to remove the air, it was charged at a cold pressure of 2.1 MPa. The stirrer was set at 500 rpm.

The reaction was started by immersing the bomb into a preheated salt bath, and the reaction temperature and time were recorded by a data logger. The heating rate was about 50°C/minute. After the reaction, the autoclave was rapidly cooled to room temperature by immersing the bomb in a cold water bath.

After reaction, all the products were acidified at a pH ≈ 2 with a HCl solution (Figure 2). The precipitates were filtered, washed and dried. Conversion of lignin to acid soluble products was calculated from these precipitates by the following equation:

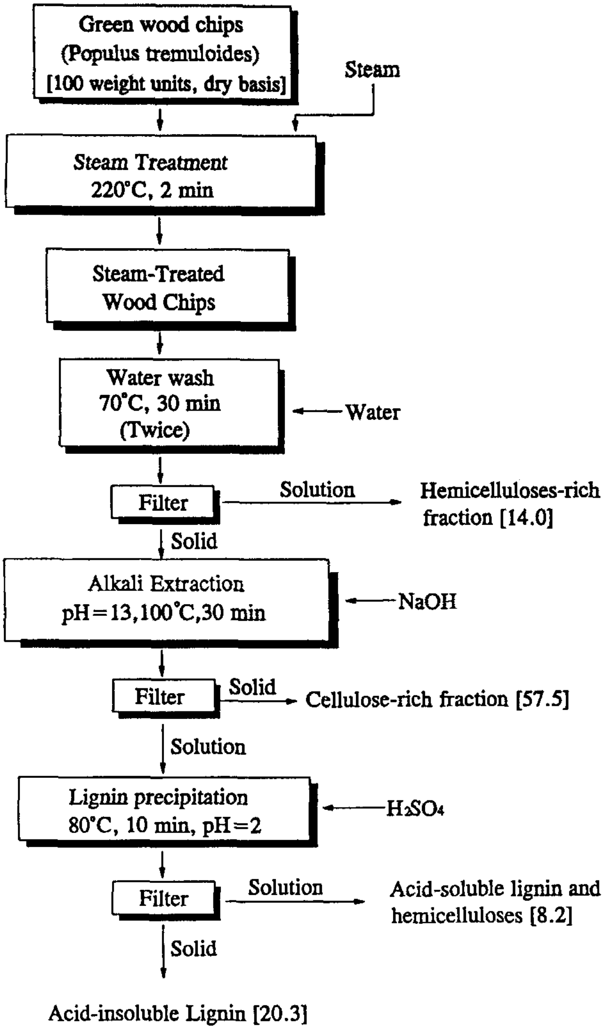

Figure 1. Block diagram of lignin production

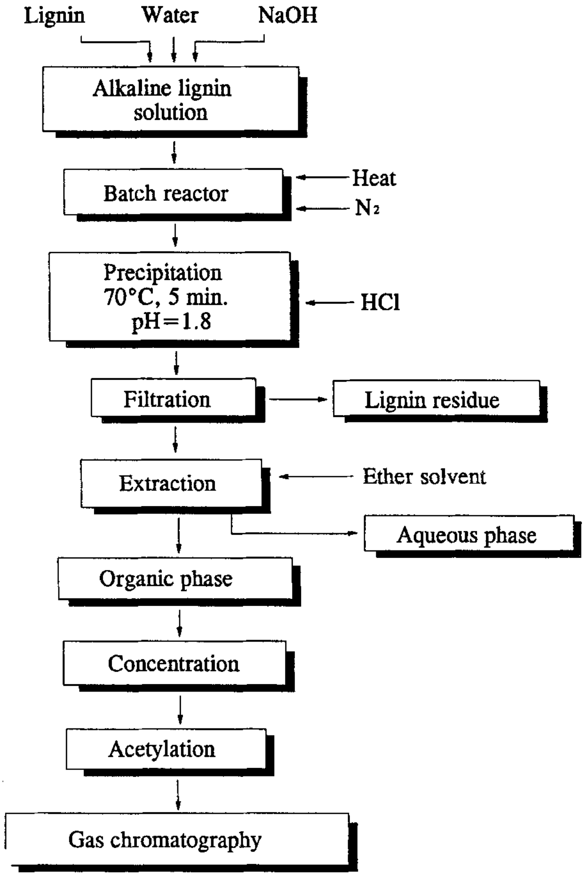

Figure 2. Scheme of lignin depolymerization

$$\text{Conversion} = [1 - W_R/W_I] * 100$$

where: W_R = weight of precipitated lignin

W_I = weight of Klason lignin in lignin materials before oxidation

The filtrate obtained after acidification was extracted with diethyl ether until the ether layer appeared colourless. After removal of the ether by evaporation under nitrogen, the ether soluble fraction was acetylated (70°C, 1 hr). The acetylated product was analyzed by capillary GC (HP Model 5890A GC) using a DB-1 column (length 30 m, ø 0.53 mm). Oven temperature was programmed from 65°C to 140°C at 6°C/min, held at 140°C for 10 min, and then heated from 140°C to 220°C at 4°C/min and held at 220°C for 10 min.

For quantitative estimation of identified compounds, response factors were calculated, using 4-ethylresorcinol as the internal standard. The relative error involved in the determination of all the compounds was ±3.8%.

A severity factor: $$Ro = \int_0^t \exp\left(\frac{T - 100}{14.75}\right) * dt$$

where t is expressed in min and T in °C, has been used to present the data (see Figures 3 to 7). The Ro factor, whose units are minutes, is a useful marker of the severity of the reaction. A thorough discussion on the significance of Ro has been presented elsewhere[7].

RESULTS AND DISCUSSION

Conversion of lignin

As seen in Figure 3, conversion of lignin can be approximated by a linear increase with severity of treatment, which indicates that high severity favours the degradation of lignin and the formation of low molecular weight compounds. The higher the severity, the higher the values of conversion. About 60% of conversion of lignin was obtained at log(Ro/min) = 7.87 (T = 350°C and t = 10 min). Similar results were obtained by Clark and Green[5] in the alkaline hydrolysis of Kraft lignin and by Thring[6] in the alkaline hydrolysis of ethylene glycol lignin.

Ratio C/O in residue

As indicated in Figure 2, a solid residue was recovered from the liquid hydrolysis products after acidification. It can be found that carbon/oxygen ratio of the residue increases rather dramatically with increasing log(Ro/min), as seen in Figure 4. This ratio can be taken as a measure of the degree of condensation, i.e., a highly condensed lignin means that it has a large number of interunit carbon-carbon bonds.

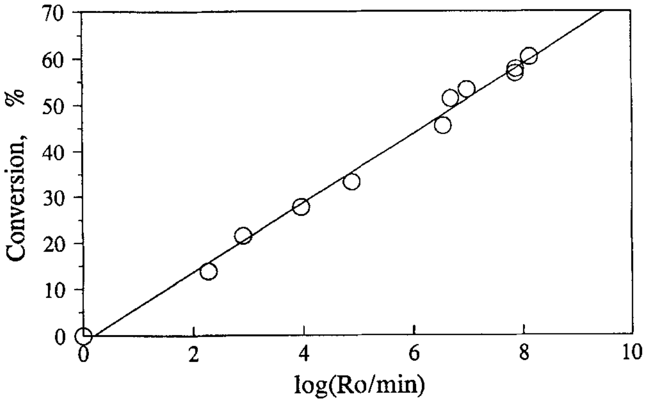

Figure 3. Conversion as a function of log(Ro/min), (NaOH: 2%)

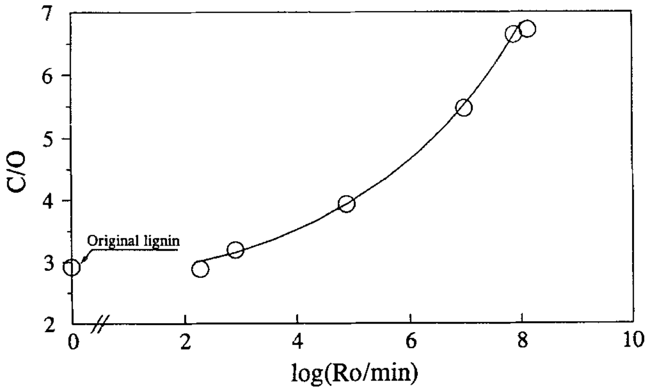

Figure 4. Ratio C/O as a function of log(Ro/min), (NaOH : 2%)

Hydrolysis products

Figure 5 shows that the quantity of ether soluble material obtained reaches maximum (20.6% of the original lignin) at log(Ro/min) = 7.87 (at a 2% NaOH concentration) and then decreases. The same trend may be observed for total identified phenols. So, high temperature favours the formation of monomeric compounds. However, further increase of treatment severity will cause the

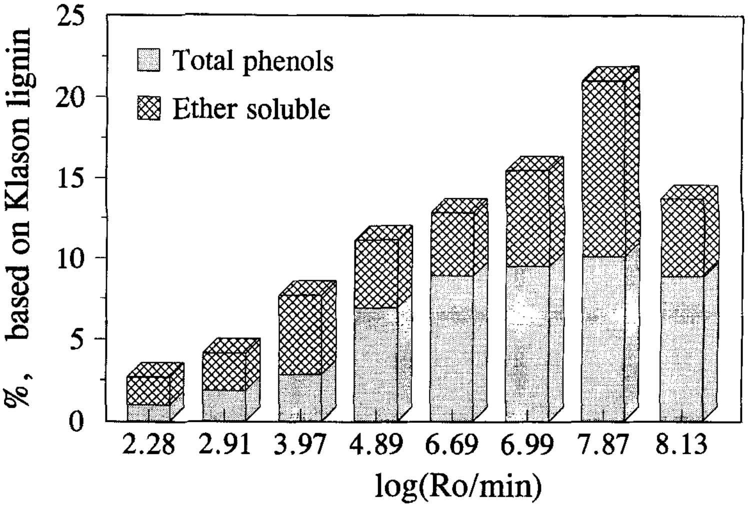

Figure 5. Ether soluble fraction and total phenols as functions of log(Ro/min), (NaOH : 2%)

decomposition of these monomers to volatile products. The maximum yield of syringol+guaiacol (at a 2% NaOH concentration) (Figure 6) occurs at lower severity (log(Ro/min) = 4.89) than that for catechols (log(Ro/min) = 7.87) (Figure 7).

Under low treatment severity, $\log_{10}$(Ro/min) ≤ 4.89, guaiacols and syringol are the principal products, which comprise up to 77% of total identified phenols or 5% of initial lignin (Figure 6) at a 2% NaOH concentration. Under low severity, there is a trace of or no catechols formed via alkaline hydrolysis. At high severity, however, such as log(Ro/min) ≥ 7, catechols begin to replace guaiacols and syringol as the most abundant monomeric products, they are about 70-90% of total identified phenols or 6-9% of initial lignin. All these results imply that there are two kinds of lignin degradation products. The primary degradation products are formed under low treatment severity via the cleavages of α- and ß- aryl ether bonds, which are phenols, guaiacols and syringol. The secondary degradation products, probably originating from primary products via the demethylation, are catechols. Sarkanen and his co-workers[8], in a kinetic study related to the alkaline hydrolysis of lignin models, also indicated that the methoxyl groups in lignin and its degradation products are generally resistant toward alkaline hydrolysis. However, they may be hydrolysed to varying degree at temperatures around 200°C.

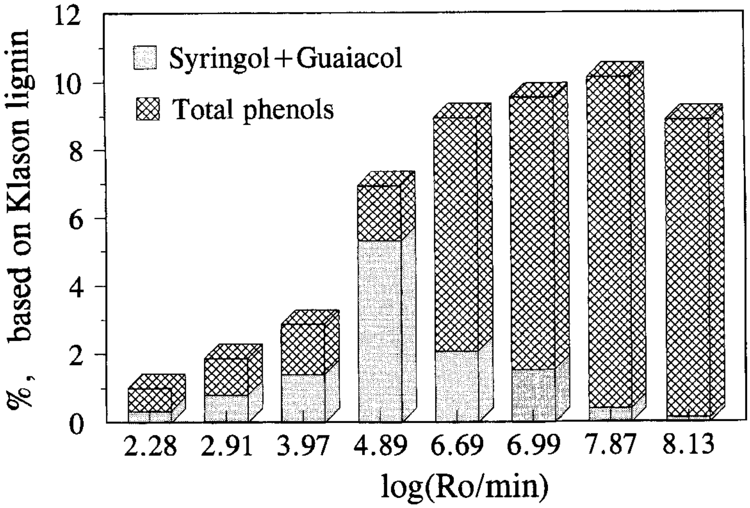

Figure 6. Total phenols and syringol+guaiacol as functions of log(Ro/min), (NaOH : 2%)

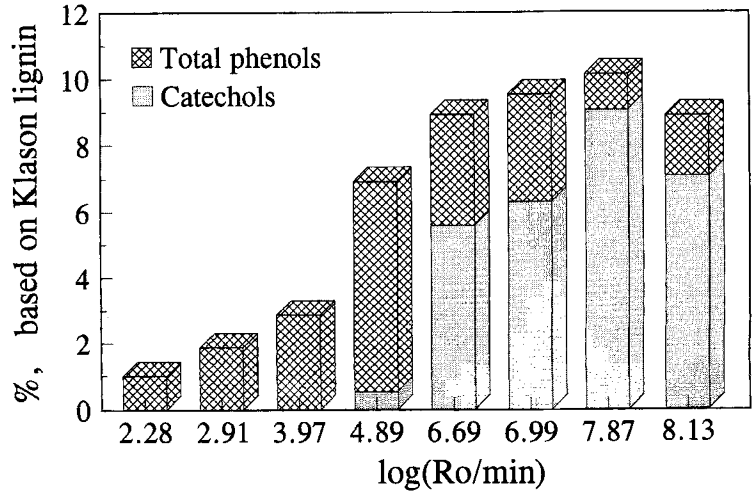

Figure 7. Total phenols and catechols as functions of log(Ro/min), (NaOH : 2%)

TABLE 1

Influence of NaOH Concentration on the Yields of Aromatic Compounds

NaOH concentration %	Ether soluble fraction %	Total phenols %	Catechols %	Syringol + Guaiacol %
0.3	15.0	9.1	2.4	5.0
1.0	16.8	10.0	6.4	1.5
2.0	20.6	10.1	8.8	0.4
7.0	17.9	7.5	4.1	0.0

Note: * All the percentages are based on the original lignin except for NaOH concentration which is based on the lignin solution.

* log (Ro/min) = 7.87

Effect of alkali concentration

The data in Table 1 indicate that the quantities of ether soluble fraction and the monomers produced vary with the sodium hydroxide concentration. They increase with increasing alkaline concentration for a log(Ro/min) = 7.87. The maximum values of 20.6% ether soluble fraction, 10.1% total identified phenols and 8.8% catechols are reached at 2% NaOH. It is also interesting to note that the yield of guaiacol+syringol reaches a maximum (5% of initial lignin) at low NaOH concentration (0.3%) and then decreases rapidly with increasing alkaline concentration. Similar phenomena were observed by Sarkanen[8] and Thring[2]. The increasing NaOH concentration favours the degradation and the demethylation of lignin and its derivatives, which promotes the formation of catechols. The high alkali concentration also speeds up the further decomposition of the monomeric compounds produced into the volatile materials.

Influence of lignin origin

Two other samples of lignin were used in our experiments. Indulin AT (Kraft softwood) lignin was obtained from Westvaco Company (Charleston, NC, USA). The second lignin sample (labelled LVS) was prepared in our laboratory by NaOH

TABLE 2

Influence of Lignin Origin on the Yield of Aromatic Compounds

Material	Conversion %	Total phenols %	Catechols %
Hardwood (LVH) lignin (*Populus tremuloides*)	16.8	10.0	6.4
Softwood (LVS) lignin (*Picea Mariana*)	14.5	9.0	5.3
Kraft softwood lignin (Indulin AT)	13.4	8.7	5.6

Note: * All the percentages are based on the original lignin.
* log (Ro/min) = 7.87, NaOH concentration = 1%

extraction from steam-exploded softwood (*Picea Mariana*). Table 2 shows that the conversion of lignin and the amount of phenols produced in alkaline hydrolysis decrease slightly in the order: hardwood (LVH) lignin > softwood (LVS) lignin > softwood (Indulin AT) lignin, which indicates the comparative reactivities of lignins of different origins to alkaline hydrolysis. Better yield of identified phenols can be obtained using hardwood (syringyl-guaiacyl) lignin as raw material than using softwood (guaiacyl) lignin.

The same phenomena were found in some reactions, such as in alkaline oxidation of lignin. In these reactions, syringyl structures were more reactive than were guaiacyl structures[9,10,11]. The differences between the lignin from the steam explosion process and the Kraft pulping process are attributed to more condensation reactions occurring during Kraft processing within lignin macromolecules. Glasser[4] had revealed that more C-C (ß-5 and ß-2) linkages and aryl-O-aryl linkages existing in Kraft lignin than the corresponding lignin obtained from steam-aqueous treatment, which indicates higher condensation degree in the former.

CONCLUSIONS

This study has demonstrated the potential of alkaline hydrolysis as a prime method of lignin degradation to monomeric compounds. To obtain the maximum yields of catechols, the conditions of the reaction have been optimized at 2% NaOH and a treatment severity (log(Ro/min) = 7.87), which corresponds to a reaction temperature of 350°C for 10 min. Under these conditions, a maximum quantity of catechols was obtained, which amounted to 9% of the initial lignin. However, the maximum quantity of syringol+guaiacol (5% of the initial lignin) could be obtained under lower severity (log(Ro/min) = 4.89) which corresponds to a reaction temperature of 230°C for 10 min.

From the data of our work, it is proposed that the hydrolysis of a steam explosion lignin undergoes two stages. Under low treatment severity, the main reactions are the cleavages of α- and ß-aryl ether bonds, which produce syringols, guaiacols and phenols as the principal products in the monomers identified. Under high severity, in addition to the cleavages of ether bonds, the demethylation is also an important reaction. Hence, catechols are the most abundant product in ether soluble materials. The lignin origins also have an influence on the alkaline hydrolysis of lignins.

To increase the reaction rate and the yields of the products desired, other specific catalysts are to be selected. Work in this direction is underway.

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