

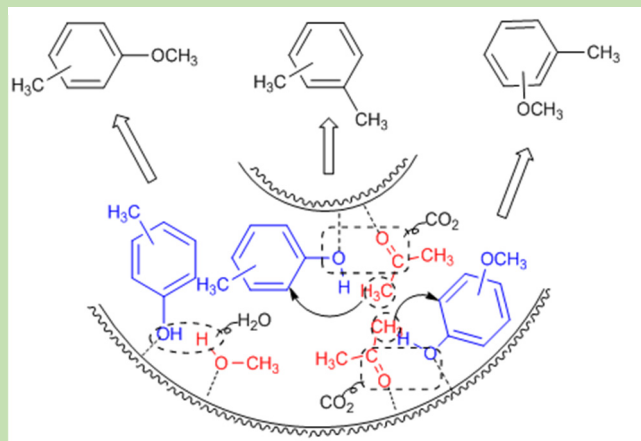


Effect of blending component on etherification of phenolic-oil over $\text{KH}_2\text{PO}_4/\text{Al}_2\text{O}_3$

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Abstract: The polarity of phenolic-oil can decrease with improved miscibility in gasoline or diesel, if the phenolic mixture can be converted to aryl ethers. As the following work of early-stage studies, in this work, based on the prior well-estimated catalyst of $\text{KH}_2\text{PO}_4/\text{Al}_2\text{O}_3$, a novel process with addition of blending component was put forward and the effects of blending components on the vapor-phase etherification of phenols with methanol were investigated systematically, using phenolic-oil as research object. Five blending components (acetic acid, formic acid, acetone, furan and ethyl acetate) were screened and the effect of



acetone was found to be the best in promoting the conversion of alkylphenols to aryl ethers. The effect of acetone dosage was examined at a constant temperature of 500 °C. It was found that the liquid recovery decreased with increasing dosage of acetone before 70wt%, and then turned to a stable trend at even higher dosages. Guaiacol or any other alkoxyphenol was not detected in all cases. Alkylphenols decreased remarkably at higher acetone dosages compared with that without blending component. Aryl ethers were most generated at the acetone dosage of 50wt%. With even higher dosage of acetone, aromatics and other compounds were more generated, leading to a remarkable decrease of aryl ethers. Furthermore, with the optimized acetone percentage of 50wt%, the influence of temperature on the alkylation reaction was investigated. It was found that the liquid recovery decreased with increasing of the temperature, and decreased even faster in the range from 500 to 550 °C. The content of aryl ethers reached to a maximum value (29.06area%) at 500 °C and aromatics were most generated (26.01area%) at 450 °C. Considering the both factors of liquid recovery and polarity of liquid product, the optimized conditions were determined as 450 °C with 50wt% of acetone dosage, with summary content of aromatics and aryl ethers (52.90area%). It was speculated that the carbonyl group of acetone interacted with the hydroxyl group of phenols, leading to the release of CO_2 , and meanwhile aromatics and ary ethers were generated from alkylphenols and alkoxyphenols respectively.

Key words: phenolic-oil; etherification; additive; acetone; methanol; catalysis

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混配组分对基于 $\text{KH}_2\text{PO}_4/\text{Al}_2\text{O}_3$ 催化剂的酚油醚化的影响

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摘要: 以 $\text{KH}_2\text{PO}_4/\text{Al}_2\text{O}_3$ 为催化剂, 针对以甲醇为烷基化试剂的酚油醚化体系, 研究了 5 种混配组分(乙酸、甲酸、丙酮、呋喃、乙酸乙酯)对酚油醚化反应规律的影响。结果表明, 丙酮对促进烷基酚转化为芳醚的作用效果最强。基于丙酮混配组分, 500 °C 下探究了丙酮质量配比的影响, 基于最佳丙酮添加量(50wt%), 进一步考察了温度对反应体系的影响, 并进行机理分析。结果表明, 丙酮含量不高于 70wt% 时, 液体收率随丙酮含量升高而降低, 进一步提高丙酮含量时液体收率基本稳定。各丙酮含量下, 液体产物中均未检出邻甲氧基苯酚或其它任何烷基酚。较高丙酮含量时烷基酚含量显著降低。丙酮含量为 50wt% 时, 芳醚含量出现极大值(29.06area%), 进一步提高丙酮含量, 芳烃及其它组分显著增加, 导致产物中芳醚含量降低。随反应温度升高, 产物中的芳醚和芳烃含量分别在 500 和 450 °C 时出现极大值。综合考虑液体收率和产物极性两方面因素, 确定该反应体系的最佳反应温度为 450 °C, 丙酮添加量为 50wt%, 最佳条件下产物中芳醚与芳烃总量达 52.90area%。丙酮分子中的羰基与酚系物中的羟基发生作用, 分解产生 CO_2 , 同时烷基酚与烷氧基酚脱羟基后分别得到芳烃和芳醚两类主要液相产物。

关键词: 酚油; 醚化; 添加剂; 丙酮; 甲醇; 催化

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1 INTRODUCTION

Bio-oil, produced from biomass pyrolysis, has huge potential to replace automobile fuels^[1-3]. However, composition of bio-oil is rather complex with abundant phenols^[4], which lead to many undesirable properties like high polarity, high corrosivity, and low heating value, etc.^[5,6] It determines that bio-oil has to be upgraded before usage^[7]. A novel method for upgradation of bio-oil via vapor-phase etherification of phenolic components with methanol^[8] was proposed, through which the polar hydroxy bond of phenols was transferred to ether group with lower polarity. The obtained aryl ethers-enriched oil could be applied as automobile fuels or components mixed with diesel or gasoline. Moreover, the addition of ethers-oil in gasoline was beneficial for enhancing the antiknock property because of the higher octane value of aryl ethers^[9].

The etherification of phenolic-oil essentially belongs to the reaction of Friedel-Crafts (F-C) alkylation. The F-C alkylation of a phenolic compound may produce O-alkylated aryl ethers (alkylation happens at the phenolic hydroxy group) or C-alkylated alkylphenols (alkylation happens at the phenolic ring). Traditional F-C alkylation is usually conducted in liquid phase, and

the catalysts of homogeneous acids such as H_2SO_4 , HF as well as AlCl_3 are frequently applied^[10]. However, the acids are hard to be recycled and the waste water is difficult to be treated. To overcome the drawbacks, gas-solid heterogeneous catalytic process is proposed. Methanol is broadly used as a methylation reagent for vapor-phase etherification of phenolic compounds, due to its low price and low toxicity, and a series of catalysts including metal oxides, phosphates, sulphates and zeolites are broadly tested^[11-15].

In previous work, phenol was used as model compound of phenolic-oil for vapor-phase alkylation reaction with methanol over activated alumina (Al_2O_3) supported catalysts^[11,16]. The results showed that $\text{KH}_2\text{PO}_4/\text{Al}_2\text{O}_3$ performed best among all tested catalysts, with good reproducibility. The conversion of phenol was up to 75.12% and anisole selectivity reached to 90.04% over $\text{KH}_2\text{PO}_4/\text{Al}_2\text{O}_3$ at 400 °C. However, when phenolic-oil was used as reactant for etherification with methanol, the content of arylethers in product oil was rather low (<32%), and even less than the content of alkylphenols (50%)^[8]. It was found that the existence of alkoxyphenols played an inhibition role to the etherification of alkylphenols, which could be partially attributed to the more prevalent adsorption of alkoxyphenols over catalyst than that of alkylphenols, and also attributed to the

formation of alkylphenols as intermediate from conversion of alkoxyphenols in prior steps of the reaction system^[9].

Considering that the etherification of phenolic-oil was still unsatisfactory, further investigations were conducted in this work, to reduce the content of phenols in product oil and meanwhile increase the concentration of aryl ethers and/or aromatics. In respect of oil polarity, the formation of aromatics was also welcome with even lower polarity than that of aryl ethers. As a following work of early-stage studies^[8,9,11], based on the prior well-estimated catalyst of $\text{KH}_2\text{PO}_4/\text{Al}_2\text{O}_3$, a novel process with addition of blending component was put forward and the effects of blending components on the vapor-phase etherification of phenols with methanol were investigated systematically in this work, using phenolic-oil as research object.

2 EXPERIMENT

2.1 Preparation of catalyst

The catalyst support was activated alumina particles

($\gamma\text{-Al}_2\text{O}_3$), its mean diameter was 1 mm. Through loading metal salt KH_2PO_4 on $\gamma\text{-Al}_2\text{O}_3$, the supported catalyst $\text{KH}_2\text{PO}_4/\text{Al}_2\text{O}_3$ was made. Firstly, $\gamma\text{-Al}_2\text{O}_3$ granules were washed using deionized water, then dried with temperature of 393 K lasting for 12 h. Thereafter, solution of KH_2PO_4 was gradually poured into $\gamma\text{-Al}_2\text{O}_3$ particles based on isopycnic impregnation rules. The impregnated $\gamma\text{-Al}_2\text{O}_3$ particles were aged at temperature of 25 °C for 24 h, further calcined at 700 °C for 8 h in a muffle furnace. Unless otherwise specified, theoretical mass loading amount of K for all supported catalysts was 10wt% (the metal weight percentage based on the mass of Al_2O_3).

2.2 Characterization of catalyst

X-ray diffraction (XRD, Smartlab, RIGAKU, Japan) with Cu $K\alpha$ radiation and a D/teX-Ultra detector was used for chemical phase analysis of $\text{KH}_2\text{PO}_4/\text{Al}_2\text{O}_3$. Figure 1 showed the XRD pattern. It was found that a new substance $\text{K}_3\text{Al}_2(\text{PO}_4)_3$ was produced due to solid phase reaction of KH_2PO_4 with Al_2O_3 after calcination at 700 °C for 8 h, besides the basis material of $\gamma\text{-Al}_2\text{O}_3$.

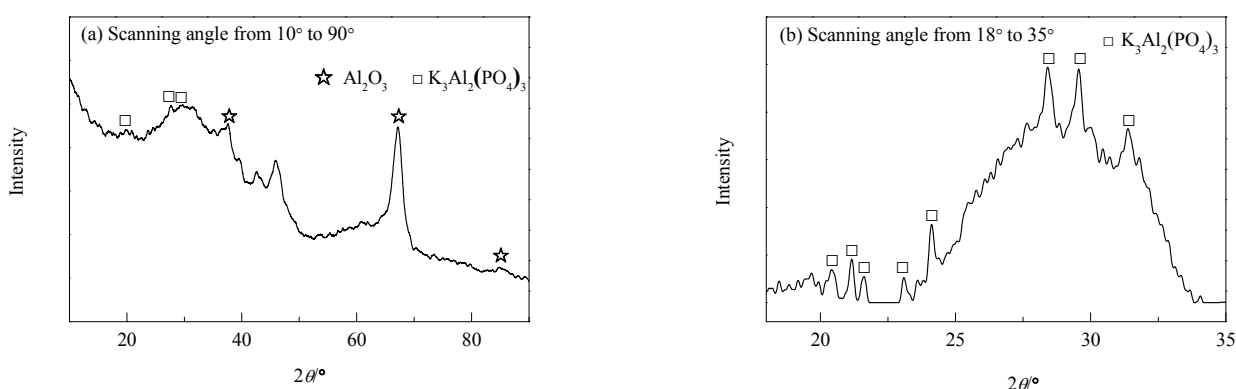


Fig.1 XRD patterns of the catalyst $\text{KH}_2\text{PO}_4/\text{Al}_2\text{O}_3$

The average pore size as well as surface area of $\text{KH}_2\text{PO}_4/\text{Al}_2\text{O}_3$ was measured by N_2 adsorption/desorption method (Tristar 3020 II adsorption instrument of Quantachrome Instrument). The total volume was determined based on T-plot curve. The surface area was obtained by BET model. Average pore diameter was calculated with BJH model. The corresponding data were showed in Table 1.

Table 1 Pore size and surface area of $\text{KH}_2\text{PO}_4/\text{Al}_2\text{O}_3$

Total pore volume/(cm^3/g)	Average pore radius/nm	Surface area/(m^2/g)
0.307	51.66	119.00

Programmed desorption of NH_3 ($\text{NH}_3\text{-TPD}$, Autochem II 2920, Micromeritics Instrument Corp, America) was applied to characterize the acid sites of catalysts. The sample was heated from room temperature to 200 °C (30 min) in He atmosphere, and then the gas mixture of NH_3 (10vol%) and He (90vol%) was introduced for adsorption of NH_3 (90 min). Thereafter, pure He was used for purging NH_3 (30 min) and the desorption curve of NH_3 varied with increasing temperature (to 700 °C with 10 °C/min) was recorded by a TCD (thermal conductivity) detector. The obtained

NH_3 -TPD curve was showed in Figure 2. It can be seen that the catalyst was mainly composed of two types of acids, with lower and middle acidity respectively.

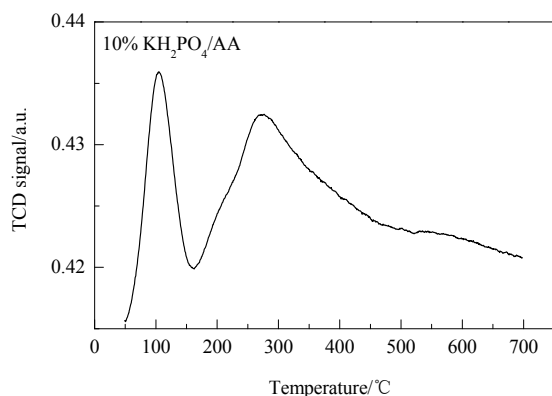


Fig.2 NH_3 -TPD analytical result of $\text{KH}_2\text{PO}_4/\text{Al}_2\text{O}_3$

2.3 Experimental procedure

The experiments on etherification of phenols with methanol were conducted under atmospheric pressure in a quartz tubular reactor. The schematic of the experimental apparatus was shown in the Figure 3. The length was 720 mm and the inner diameter was 24 mm for this fixed-bed reactor. There was an electric furnace equipped in the reactor for heating. Once the catalyst bed temperature increased to a setting point, N_2 as the carrier gas (55 mL/min) was introduced into the reactor to eliminate air for 10 min. Then liquid mixture of phenols and methanol with and without existence of a blending component was fed in by peristaltic pump. The liquid reactant was vaporized first and further converted to products when contacting with the catalyst bed. Carrier gas would carry the gas product out of the fixed bed

reactor. After that, the products condensed to liquid in the condensing unit, which contained a Graham condenser and three glass bottles placed in a cold trap. Unless otherwise specified, the following reaction conditions were kept constant in all tests: the catalyst loading amount was 15 g, the feeding rate of reactant mixture was 0.067 mL/min with time on stream of 3 h.

2.4 Product analysis

After experiment, the mass of liquid product was weighted. In addition, QP2020 Gas Chromatography with Mass Spectrometry (GC-MS, DB-FFAP column 30 mm \times 0.25 mm \times 0.25 μm , SHIMADZU, Japan) was applied to analyze the liquid product. The oven temperature started from 40 $^{\circ}\text{C}$ (5 min), then increased to 100 $^{\circ}\text{C}$ (3 min) by 5 $^{\circ}\text{C}/\text{min}$, and finally was raised to 240 $^{\circ}\text{C}$ (1 min) by 5 $^{\circ}\text{C}/\text{min}$. The inlet temperature and the ion source temperature were 240 and 200 $^{\circ}\text{C}$ respectively. The gas product was firstly collected using gas bag, then analyzed using GC (Gas Chromatography) equipped with three Micro GC 3000 TCD detectors (INFICON, Switzerland).

To evaluate the reliability of the experimental system, the etherification of phenol with methanol (molar ratio of 1:5) over $\text{KH}_2\text{PO}_4/\text{Al}_2\text{O}_3$ at 400 $^{\circ}\text{C}$, as representative experiment was conducted three times. The results demonstrated that the experimental results were reliable with the standard deviation of phenol conversion of 1.31wt% and the anisole selectivity of 0.75area%.

3 RESULTS AND DISCUSSION

3.1 Conversion of phenolic-oil without blending component

The etherification of a raw phenolic-oil free of alkoxyphenol was tested at 450 $^{\circ}\text{C}$ over $\text{KH}_2\text{PO}_4/\text{Al}_2\text{O}_3$, methanol was used as alkylation agent and added as the same mass with phenolic-oil (1:1 in mass basis). Raw alkoxyphenol-free phenolic-oil was produced from slow and long-time pyrolysis of straw (Beijing Sanju Environmental Protection & New Materials Co., Ltd.), as alkoxyphenols with lower stability tend to be converted more easily through a long-time thermal treatment. The experimental data were compared with the results from conversion of the same phenolic-oil with addition of

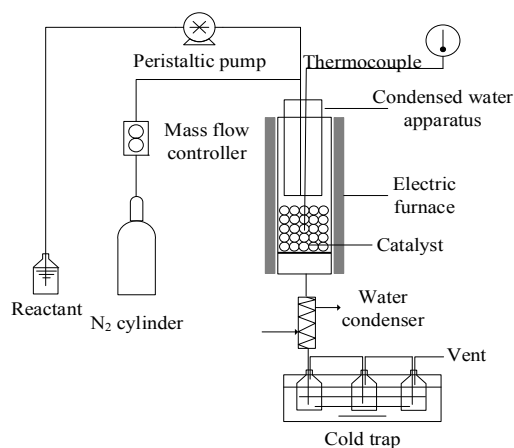


Fig.3 Experimental system for conversion of phenolic-oil

guaiacol (a typical alkoxyphenol) under same conditions. The main components of the raw phenolic-oil and the product oils from conversions of the phenolic-oil without and with addition of guaiacol were showed in Table 2. The corresponding total ion chromatographs (TICs) of the three samples were showed in Figure 4.

The raw phenolic-oil was predominantly composed of alkylphenols (60.46area%), with some minor components such as aromatics, water, acetic acid, etc., while no alkoxyphenols were detected. In the products

from conversion of the raw alkoxyphenol-free phenolic-oil, the content of alkylphenols was remarkably decreased (23.18area%), and meanwhile aryl ethers (57.77area%) were much produced. By contrast, products from alkylation of phenolic-oil with addition of guaiacol, the content of alkylphenols was still rather higher (40.95area%). Aryl ethers were produced much less (22.63area%) and acetic acid disappeared, while aromatics were relatively more generated (10.90area%). It verified the inhibition effect of alkoxyphenol to the

Table 2 Components of raw phenolic-oil, products from conversion of the alkoxyphenol-free phenolic-oil and products from conversion of the phenolic-oil with addition of guaiacol

Classification	Number	Substance	Peak area/%		
			Raw phenolic-oil	Product from conversion of the alkoxyphenol-free phenolic-oil	Product from conversion of the phenolic-oil with addition of guaiacol
Alkylphenol	A1	Phenol, 2,3-dimethyl	1.53	1.62	1.26
	A2	Phenol	19.86	—	—
	A3	Phenol, 4-methyl-	12.1	—	—
	A4	Phenol, 3-methyl-	5.49	1.01	2.36
	A5	Phenol, 4-ethyl-	11.26	0.35	5.78
	A6	Phenol,2-methyl-	—	5.25	10.52
	A7	Phenol, 3,4-dimethyl	1.42	4.00	7.24
	A8	Phenol,2-(1-methylethyl)-	—	1.95	2.72
	A9	Phenol,5-(1-methylethyl)-	—	1.75	—
	A10	Phenol,2-methoxy-4-methyl-	—	—	7.52
	A11	Phenol,2-methoxy-6-methyl-	—	—	2.25
	A12	All other alkyl phenols	8.80	7.25	1.3
Aryl ether	B1	Benzene, methoxy-	—	10.25	4.97
	B2	Benzene, 1-methoxy-2-methyl-	—	6.58	3.04
	B3	Benzene, 1-methoxy-4-methyl-	—	6.92	3.54
	B4	Benzene,1-methoxy-3-methyl-	—	4.16	2.29
	B5	Benzene,2-methoxy-1,4-dimethyl-	—	8.90	—
	B6	Benzene, 1-ethyl-4-methoxy-	—	9.30	5.84
	B7	Benzene, 1-methoxy-4-(1-methylethyl)-	—	4.61	2.3
	B8	All other aryl ethers	0	7.05	0.65
Aromatic hydrocarbon	C1	Naphthalene	2.98	3.18	3.73
	C2	Naphthalene, 2-methyl-	1.64	1.99	2.71
	C3	Naphthalene, 1-methyl-	1.17	1.59	2.05
	C4	All other aromatic hydrocarbons	7.49	4.04	2.41
Other	D1	Water	4.01	2.85	3.82
	D2	Acetic acid	5.51	—	—

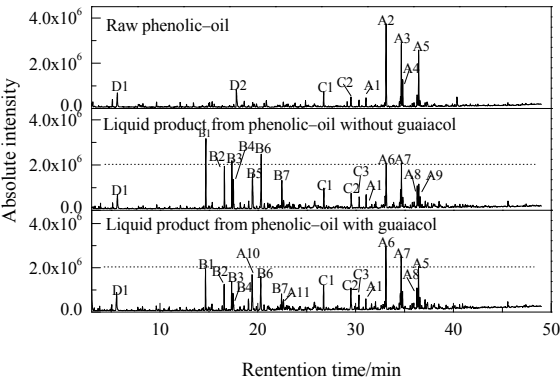


Fig.4 TICs of raw phenolic-oil, products from alkylation of the alkoxyphenol-free phenolic-oil and products from alkylation of the phenolic-oil with addition of guaiacol

conversion of alkylphenol. The data will be used as a reference for evaluating the role of a blending component in improving conversions of alkylphenols and the selectivity to aryl ethers and/or aromatics.

3.2 Conversion of the guaiacol-added phenolic-oil with blending component

The guaiacol-added phenolic-oil was used as research object for screening of blending components. In all experiments, the ratio of methanol to guaiacol to phenolic oil was 1:0.1:1 in mass basis. The roles of 5 blending components (acetic acid, formic acid, acetone, furan, ethyl acetate) were examined at 500 °C over

$\text{KH}_2\text{PO}_4/\text{Al}_2\text{O}_3$, and the mass ratio of the blending component to the phenolic-oil/guaiacol/methanol mixture was kept constant (30wt%) in all tests. The liquid recovery (the mass ratio of the liquid received after reaction to the total liquid introduced to the system), as well as the contents of main products were listed in table 3. It showed that the liquid recoveries were all gotten decreased in different degrees with the existence of blending component, which may be attributed to the formation of gas or solid product promoted under the role of blending component over $\text{KH}_2\text{PO}_4/\text{Al}_2\text{O}_3$. The added

guaiacol disappeared completely in all cases. Comparatively, the liquid recovery was relatively higher under the role of acetone, with a highest selectivity to aryl ethers (26.07area%). When ethyl acetate was used as the blending component, the content of alkylphenols in product oil was the lowest (40.62area%) with relatively higher content of aromatics (25.65area%). Therefore, in the following work, the influences of the two blending components of acetone and ethyl acetate were further investigated.

Table 3 Effect of blending components on the conversion of guaiacol-added phenolic-oil with product selectivity

Substance	Liquid recovery/wt%	Selectivity/area%			
		Alkyl phenol	Aryl ether	Aromatic	Other
None	70.97	46.60	22.28	17.92	13.18
Acetic acid	63.76	41.14	17.39	24.50	16.97
Formic acid	60.13	49.19	14.16	23.58	13.07
Acetone	67.90	42.24	26.07	16.22	15.47
Furan	58.94	43.25	17.92	23.88	14.96
Ethyl acetate	65.72	40.62	16.37	25.65	17.39

3.3 Dosage effect of acetone and ethyl acetate on the conversion of the guaiacol-added phenolic-oil

The effect of acetone dosage was tested at 500 °C over $\text{KH}_2\text{PO}_4/\text{Al}_2\text{O}_3$ using the same guaiacol-added phenolic-oil (methanol:guaiacol:phenolic-oil=1:0.1:1) as reactant. The mass ratio of acetone to the solution was set as 10wt%, 30wt%, 50wt%, 70wt% and 90wt% respectively. The liquid recovery and the composition of liquid product (the contents of acetone and methanol were excluded), as well as the gas yield with gas composition (mass fraction), were presented in Figure 5. The experimental results demonstrated that the liquid recovery deceased with increasing dosage of acetone before 70wt%, and then turned to a stable trend at even higher dosages. Guaiacol or any other alkoxyphenol was not detected in all cases. Alkylphenols were remarkably decreased at higher acetone dosages compared with that without addition of blending component. The content of aryl ethers increased with increasing dosage of acetone firstly, and then declined after reaching to maximum value at the dosage of 50wt%. It indicated that the addition of acetone can certainly promote the formation of aryl ethers from the enhanced conversion of alkylphenols, but merely in middle dosages. With even higher dosage of acetone, aromatics and other

compounds were more generated, leading to a remarkable decrease of aryl ethers. The gas product was mainly composed of CH_4 , CO and CO_2 . The concentration of CH_4 was generally steady with varied dosage of acetone. CO_2 was more generated with the addition of acetone, while the concentration of CO just illustrated an opposite trend. The yield of gas product slightly decreased with the addition of acetone, which indicated that the decrease of liquid recovery was mainly caused by a promoted formation of solid residue, rather than the product of gases.

The effect of dosage of ethyl acetate was also investigated under the same conditions as that blended with acetone (500 °C over $\text{KH}_2\text{PO}_4/\text{Al}_2\text{O}_3$). The mass ratio of ethyl acetate to the solution was set as 10wt%, 30wt%, 50wt% respectively. The results were summarized in Figure 6. From Figure 6, it was known that liquid recovery deceased with increasing of ethyl acetate dosage in the range of 10wt%~50wt%. The composition of liquid product was generally stable under different dosages of ethyl acetate. Guaiacol disappeared in all temperatures. Alkylphenols decreased, but in a lower degree compared with that blended with acetone. Aromatics were more generated with the increase of ethyl acetate, whereas aryl ethers were decreased contrarily in

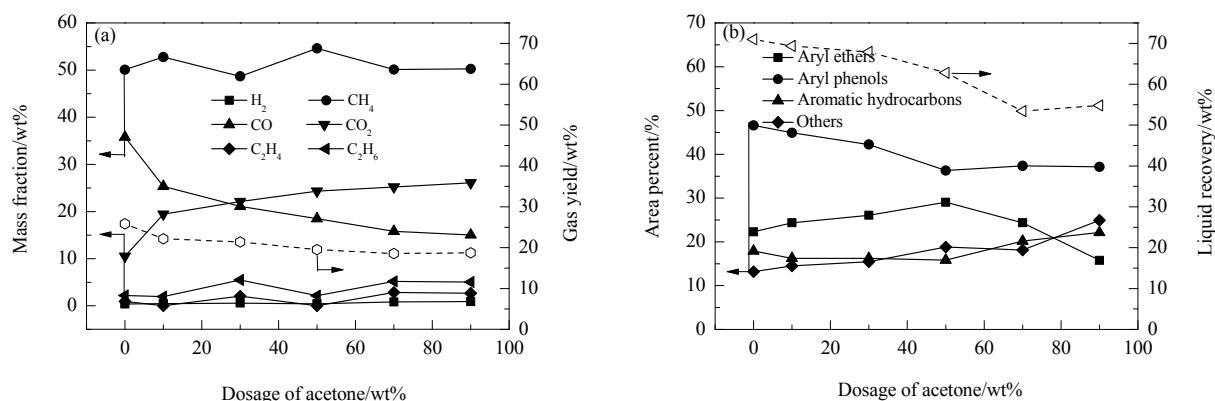


Fig.5 Influence of the dosage of acetone on the conversion of the guaiacol-added phenolic-oil

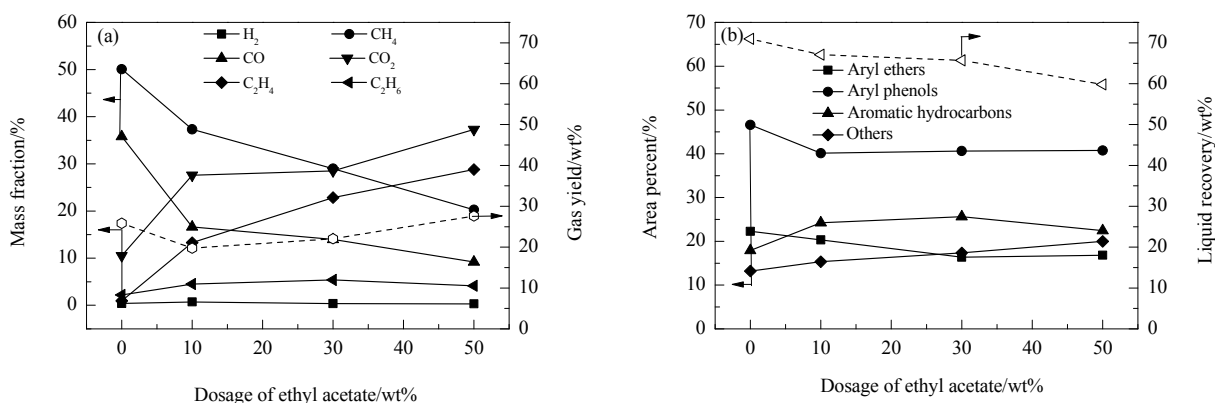


Fig.6 Influence of the dosage of ethyl acetate dosage on the conversion of the guaiacol-added phenolic-oil

a similar degree. The gas yield decreased with addition of ethyl acetate firstly and then turned to an increasing trend in higher dosages. The concentrations of CH_4 and CO decreased with increasing dosage of ethyl acetate monotonously, while CO_2 and C_2H_4 were both remarkably more generated with the addition of ethyl acetate. It can be speculated that CO_2 and C_2H_4 were generated from the decomposition of ethyl acetate over $\text{KH}_2\text{PO}_4/\text{Al}_2\text{O}_3$. The remained two species of H and CH_3 in ethyl acetate combined with the OH group and the aromatic ring of phenols respectively, leading to the release of H_2O and the formation of methylbenzenes. The loss of OH from phenols restricted the formation of aryl ethers and meanwhile augmented the yield of aromatics. The speculated schematic mechanism was showed in Figure 7.

In general, compared between the effects of acetone and ethyl acetate, the addition of acetone as blending component was more preferred, considering that arylethers were more generated, with even lower content of alkylphenols in product under the role of acetone. In the following work, the influence of temperature with

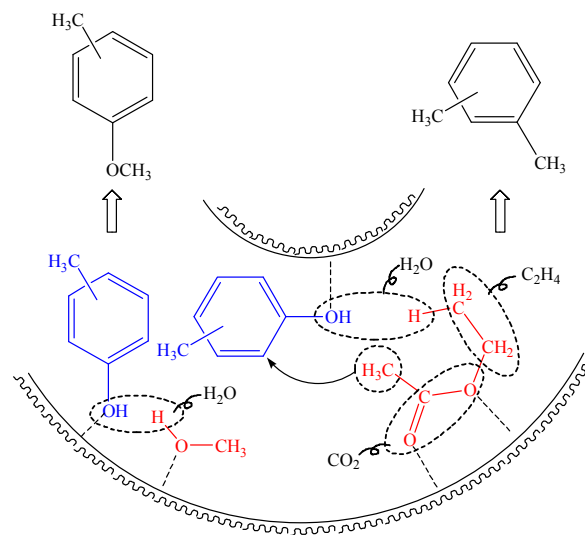


Fig.7 Schematic mechanism on the role of ethyl acetate

addition of acetone was further investigated.

3.4 Effect of temperature on conversion of the guaiacol-added phenolic-oil with addition of acetone

On the basis of the prior optimized dosage of acetone (50wt%), the reaction temperature was further investigated over $\text{KH}_2\text{PO}_4/\text{Al}_2\text{O}_3$, using the same

guaiacol-added phenolic-oil as reactant (methanol:guaiacol:phenolic-oil=1:0.1:1). The results showed that liquid recoveries and composition of liquid products, as well as the yield of gas product with gas composition (mass fraction), were showed in Figure 8. From Figure 8, liquid recovery decreased with the increase of temperature, and decreased even faster in the range from 500 to 550 °C. The yield of gas product increased slightly with increasing temperature, indicating that a higher temperature benefited the formation of gases. The main gas components were CH₄, CO, CO₂. The concentration of CH₄ increased with increasing temperature in lower temperatures and then became stable after 500 °C. CO₂ was most generated at the lowest temperature of 400 °C but decreased with rising

temperature rapidly, while the concentration of CO illustrated rising trends contrarily. Guaiacol disappeared in all temperatures. The content of aryl ethers increased with increasing temperature in early stage, while turned to a reducing trend after reaching to the maximum value (29.06area%) at 500 °C. Aryl ethers were usually heat sensitive, and thus hard to be more generated at higher temperatures. The content of alkylphenols increased with the increase of temperature monotonously in the range of 400~550 °C, which verified the prevalence of C-alkylation process at higher temperatures. Aromatics were most generated at the lower temperature of 450 °C. The contents of others were highest at the lowest temperature of 400 °C, but decreased rapidly at 400~500 °C then slightly decreased at high temperature.

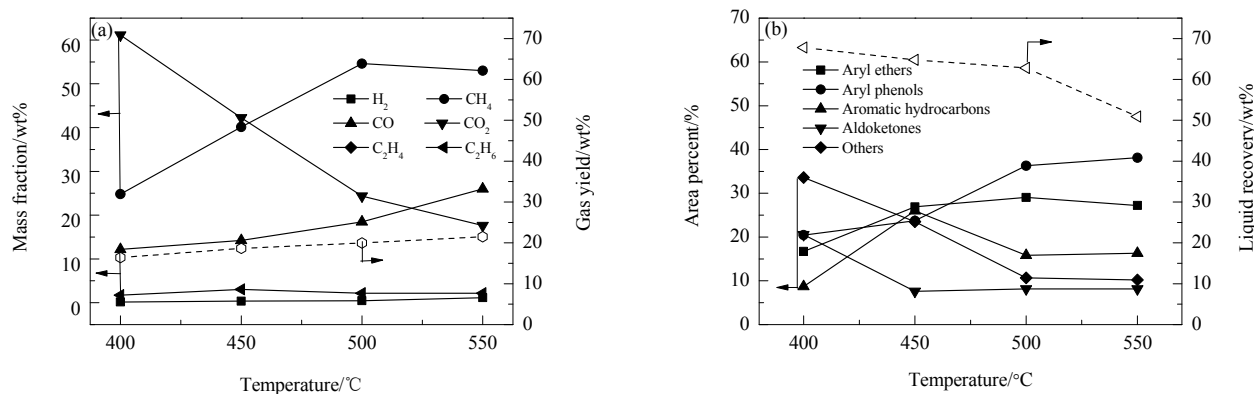


Fig.8 Effects of temperatures on conversion of guaiacol-added phenolic-oil blended with 50wt% acetone

In general, under the effect of acetone, aryl ethers were most generated (29.06area%) at 500 °C, while the maximum summary content of aryl ethers and aromatics (52.90area%) appeared at 450 °C, with a higher liquid recovery (64.78wt%) and less alkylphenols in product (23.71area%). Considering that aromatics had even lower polarity than aryl ethers, the proper reaction temperature was therefore determined as 450 °C.

To make a further insight of the product selectivity, the TICs of the products from conversions of the guaiacol-added phenolic-oil without blending component, and the one mixed with acetone at 500 °C were respectively showed in Figure 9. Table 4 gave the detailed product composition.

It can be seen that under the role of acetone, the alkylphenols with polymethyl groups including A1, A2, A8, A9 and A10 decreased remarkably, similarly, the

aromatics with polymethyl groups such as C2 and C5 decreased particularly even to zero level, meanwhile, the aryl ethers of B8 and B9, and the other components of water and D3 increased obviously with the addition of acetone.

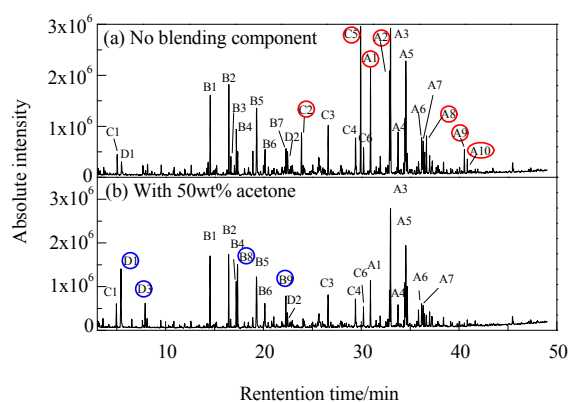


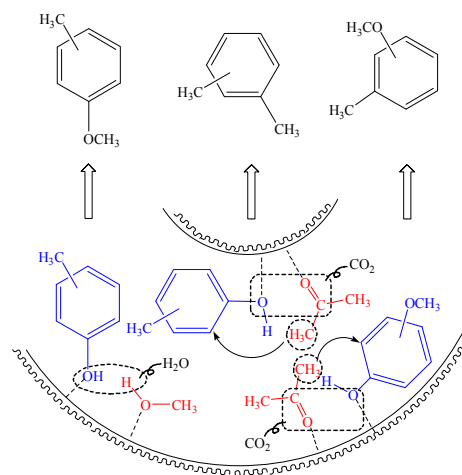
Fig.9 TICs of products from conversions of guaiacol-added phenolic-oil with no blending component and the one mixed with 50wt% acetone

Table 4 Compositions of the products from conversions of the guaiacol-added phenolic-oil with no blending component and the one mixed with acetone

Classification	Number	Substance	Peak area/%	
			(a)	(b)
Alkyl phenols	A1	Phenol, 2,6-dimethyl-	5.65	2.87
	A2	Phenol, 2,3,5-trimethyl-	5.46	2.20
	A3	Phenol, 2-methyl-	9.78	9.03
	A4	Phenol, 2,4,6-trimethyl-	2.13	1.39
	A5	Phenol, 3,4-dimethyl	6.59	5.44
	A6	Phenol, 2-(1-methylethyl)-	1.89	1.45
	A7	Phenol, 3-ethyl-	1.87	1.40
	A8	Phenol, 2,3,5,6-tetramethyl-	1.98	0.88
	A9	Phenol, 2-(1,1-dimethylethyl)-3-methyl-	1.29	—
	A10	Phenol, 5-methyl-2-(1-methylethyl)-	0.71	—
	A11	All other alkyl phenols	9.25	10.45
Aryl ethers	B1	Benzene, methoxy-	4.09	4.19
	B2	Benzene, 1-methoxy-2-methyl-	4.42	4.23
	B3	Benzene, 2-methoxy-1,3-dimethyl-	0.89	0.46
	B4	Benzene, 1-methoxy-4-methyl-	2.27	2.62
	B5	Benzene, 4-methoxy-1,2-dimethyl-	5.45	5.43
	B6	Benzene, 1-ethyl-4-methoxy-	1.92	2.32
	B7	Benzene, 1-methoxy-4-(1-methylethyl)-	1.53	—
	B8	Benzene, 1-methoxy-3-methyl-	—	3.75
	B9	Benzene, 2-methoxy-1,3,5-trimethyl-	—	2.35
	B10	All other aryl ethers	1.84	3.71
Aromatic hydrocarbons	C1	Benzene, methyl-	1.18	1.59
	C2	Benzene, pentamethyl-	2.28	—
	C3	Naphthalene	2.49	2.28
	C4	Naphthalene, 2-methyl-	2.06	1.88
	C5	Benzene, hexamethyl-	8.41	—
	C6	Naphthalene, 1-methyl-	1.49	1.18
	C7	All other aromatic hydrocarbons	5.01	9.79
Other	D1	Water	0.77	5.73
	D2	Benzofuran, 2-methyl-	1.91	—
	D3	3-Penten-2-one, 4-methyl-	—	1.64

Based on the phenomena and regulations related to the influence of acetone on the composition of gaseous and liquid products, the mechanic role of acetone was speculated. The mechanism diagram was showed in Figure 10. Considering that there was only one oxygen atom in the molecule of acetone, the decomposition of acetone should mainly produce CO rather than CO_2 , but in fact CO_2 was more generated with the addition of acetone, as shown in Figure 5. It indicated that the decomposition of acetone must be interacted with some other oxygenated compound. It was speculated that the carbonyl group of acetone interacted with the hydroxyl group of phenols, leading to the release of CO_2 . Meanwhile, aromatics and aryl ethers were generated respectively from alkylphenols and alkoxyphenols. The activation of alkylphenols or alkoxyphenols over $\text{KH}_2\text{PO}_4/\text{Al}_2\text{O}_3$ may vary with different temperatures. It seemed that the activation of alkoxyphenols was more

prevalent than that of alkylphenols at 500°C and thus ary ethers were more generated than aromatics, while the activations of alkylphenols and alkoxyphenols were evenly matched at 450°C and thus gave equal contents of aromatics and ary ethers, as Figure 8 illustrated.

**Fig.10** Schematic mechanism on the role of acetone

4 CONCLUSIONS

The vapor-phase alkylation of phenolic-oil with methanol was studied over $\text{KH}_2\text{PO}_4/\text{Al}_2\text{O}_3$. A novel approach with addition of blending component was put forward and examined systemically. The main conclusions are listed as follows:

(1) The effects of five blending components (acetic acid, formic acid, acetone, furan, ethyl acetate) were screened and acetone was found to be the best in promoting the conversion of alkylphenols to aryl ethers.

(2) The effect of dosage acetone was further examined at 500 °C. It was found that the liquid recovery deceased with increasing dosage of acetone before 70wt%, and then turned to a stable trend at even higher dosages. Guaiacol or any other alkoxyphenol was not detected in all cases. Alkylphenols decreased remarkably at higher acetone dosages compared with that without blending component. Aryl ethers were most generated (29.06area%) at the dosage of 50wt%. With even higher dosage of acetone, aromatics and other compounds were more generated, leading to a remarkable decrease of aryl ethers. When ethyl acetate was used as blending component, aromatics were more generated, whereas aryl ethers decreased contrarily in a similar degree. Therefore, the addition of 50wt% acetone as blending component was more preferred.

(3) With the acetone percentage of 50wt%, the influence of temperature on etherification of phenolic-oil was further investigated. The liquid recovery deceased with increasing temperature, and decreased even faster in the range from 500 to 550 °C. Aryl ethers and aromatics were separately most generated at 500 and 450 °C respectively. Considering the both factors of liquid recovery (64.78wt%) and summary content of aryl ethers and aromatics (52.90are a%), the optimized conditions were determined as 450 °C with 50wt% of acetone dosage.

(4) It was speculated that the carbonyl group of acetone interacted with the hydroxyl group of phenols, leading to the release of CO_2 . Meanwhile, aromatics and arylethers were generated from alkylphenols and alkoxyphenols respectively.

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