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SYNTHESIS AND CHARACTERIZATION OF AROMATIC ALCOHOLS FROM THE C9 AROMATIC FRACTION OF PYROLYSIS DISTILLATE USING H- ZSM-5 CATALYST

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Abstract. This study investigates the conversion of a C9 monoaromatic fraction isolated from pyrolysis distillate into aromatic alcohols using formaldehyde and H-ZSM-5 zeolite as a heterogeneous catalyst. The reaction was carried out using 39% formalin at an aromatic compound-to-formaldehyde molar ratio of 1:1 and a temperature of 140-150 °C for 4 h. A maximum product yield of 92% was obtained under the applied conditions. The synthesized product was characterized by gas chromatography–mass spectrometry (GC-MS) and Fourier-transform infrared (FTIR) spectroscopy. GC-MS analysis revealed that the product predominantly consisted of 1-Phenylpropanol-(1) (73.16 Area%) and Benzenemethanol, α,α -dimethyl- (26.30 Area%), with a combined relative abundance of 99.46%. FTIR analysis further confirmed the presence of hydroxyl-containing aromatic structures through characteristic O-H, aromatic C-H, and C-O absorption bands. The results demonstrate the potential of pyrolysis-derived C9 aromatic hydrocarbons as feedstocks for the production of value-added aromatic alcohols.

Keywords: pyrolysis distillate, C9 aromatic fraction, aromatic alcohols, H-ZSM-5, formaldehyde.

Annotatsiya. Ushbu tadqiqotda piroliz distillyatidan ajratib olingan C9 monoaromatik fraksiyani formaldegid va geterogen katalizator sifatida H-ZSM-5 seoliti ishtirokida aromatik spirtlarga aylantirish jarayoni o‘rganildi. Reaksiya 39% li formalin eritmasidan foydalanilgan holda, aromatik birikma va formaldegidning 1:1 mol nisbatida, 140-150 °C haroratda 4 soat davomida olib borildi. Qo‘llanilgan sharoitlarda mahsulotning maksimal unumi 92% ni

tashkil etdi. Sintez qilingan mahsulot gaz xromatografiya-mass-spektrometriya (GC-MS) va Furiye transformatsiyali infraqizil spektroskopiya (FTIR) usullari yordamida tavsiflandi. GC-MS tahlili natijasida mahsulotning asosiy komponentlari 1-Phenylpropanol-(1) (73,16 Area%) va Benzenemethanol, α,α -dimethyl- (26,30 Area%) ekanligi aniqlandi va ularning umumiy nisbiy ulushi 99,46% ni tashkil etdi. FTIR tahlili O–H, aromatik C–H va C–O bog‘lariga xos yutilish polosalari orqali gidroksil guruhlarini saqlovchi aromatik strukturalar hosil bo‘lganini qo‘shimcha tasdiqladi. Olingan natijalar pirolizdan hosil bo‘lgan C9 aromatik uglevodorodlardan yuqori qo‘shilgan qiymatga ega aromatik spirtlar olish uchun xomashyo sifatida foydalanish imkoniyatini ko‘rsatadi.

Kalit so‘zlar: piroliz distillyati, C9 aromatik fraksiya, aromatik spirtlar, H-ZSM-5, formaldegid

Аннотация. В данной работе исследовано превращение выделенной из пиролизного дистиллята моноядерной ароматической фракции C9 в ароматические спирты с использованием формальдегида и цеолита H-ZSM-5 в качестве гетерогенного катализатора. Реакцию проводили с использованием 39%-ного формалина при мольном соотношении ароматического соединения к формальдегиду 1:1 и температуре 140-150 °C в течение 4 ч. В применяемых условиях максимальный выход продукта составил 92%. Полученный продукт исследовали методами газовой хроматографии-масс-спектрометрии (ГХ-МС) и инфракрасной спектроскопии с преобразованием Фурье (FTIR). Согласно результатам ГХ-МС, основными компонентами продукта являлись 1-Phenylpropanol-(1) (73,16 Area%) и Benzenemethanol, α,α -dimethyl- (26,30 Area%), суммарная относительная доля которых составила 99,46%. Данные FTIR также подтвердили наличие ароматических структур, содержащих гидроксильные группы, по характерным полосам поглощения O–H, ароматических C–H и C–O связей. Полученные результаты демонстрируют перспективность использования C9 ароматических углеводородов пиролизного происхождения в качестве сырья для получения ароматических спиртов с высокой добавленной стоимостью.

Ключевые слова: пиролизный дистиллят, C9 ароматическая фракция, ароматические спирты, H-ZSM-5, формальдегид

INTRODUCTION. Pyrolysis is an important industrial process for the production of lower olefins, particularly ethylene, propylene, and butene-1 [1]. Depending on the feedstock, such as ethane, propane–butane, gas condensate, or naphtha, the process generates not only the desired olefin products but also pyrolysis condensate as a valuable secondary product [2]. Pyrolysis distillate, one of the main fractions of pyrolysis condensate, contains a considerable proportion of aromatic hydrocarbons and therefore represents a promising feedstock for further chemical conversion and the production of value-added compounds [3].

The aromatic fraction of pyrolysis distillate consists predominantly of monoaromatic hydrocarbons, including alkyl-substituted benzenes and other aromatic compounds [4]. Among these components, C9 monoaromatic hydrocarbons are of particular interest because their molecular structures provide suitable starting materials for further functionalization [5]. The selective recovery of C9 aromatic compounds from pyrolysis-derived streams can

therefore contribute to the more efficient utilization of secondary petrochemical products and provide an alternative feedstock for the synthesis of oxygen-containing aromatic compounds [6].

Functionalization of aromatic hydrocarbons is an important strategy for increasing the chemical value and applicability of hydrocarbon feedstocks [7]. In particular, the conversion of aromatic hydrocarbons into aromatic alcohols introduces a reactive hydroxyl group into the molecular structure, significantly expanding their potential applications as intermediates in organic synthesis. Formaldehyde-based functionalization represents one possible approach for introducing hydroxymethyl groups into aromatic substrates [8]. The efficiency and selectivity of such reactions depend strongly on the catalyst type, reaction temperature, reactant ratio, and reaction time [9].

Zeolite catalysts have attracted considerable attention in heterogeneous organic synthesis because of their well-defined pore structures and acidic active sites. H-ZSM-5, in particular, possesses Bronsted and Lewis acid sites that can promote transformations of aromatic compounds and facilitate reactions involving formaldehyde [10]. Its heterogeneous nature also provides practical advantages in product-catalyst separation compared with conventional homogeneous acid catalysts. Consequently, the application of H-ZSM-5 for the functionalization of C9 aromatic fractions obtained from pyrolysis distillate is of considerable interest.

An important challenge in the conversion of a multicomponent C9 aromatic fraction is the identification of the individual products formed during the reaction. Since the starting fraction contains several aromatic hydrocarbons with different substitution patterns, the resulting product may also consist of a mixture of structurally related aromatic alcohols [11]. Therefore, reliable characterization of the reaction product is essential. Gas chromatography–mass spectrometry (GC–MS) provides information on the qualitative and relative quantitative composition of the product, while Fourier-transform infrared spectroscopy (FTIR) enables confirmation of the characteristic functional groups formed during the reaction [12].

MATERIALS AND METHODS

Preparation of the C9 aromatic fraction

Pyrolysis distillate obtained as a secondary product of the pyrolysis process was used as the initial hydrocarbon feedstock. The pyrolysis distillate contained predominantly monoaromatic hydrocarbons together with sulfur-containing organic compounds. Prior to the isolation of the C9 aromatic fraction, the feedstock was subjected to alkaline treatment to remove sulfur-containing compounds, primarily hydrogen sulfide and mercaptans.

For alkaline purification, a 20% aqueous sodium hydroxide (NaOH) solution was used. The pyrolysis distillate was cooled to approximately room temperature and contacted with the alkaline solution in a laboratory extraction column. After intensive contact between the two phases, the mixture was allowed to separate. The hydrocarbon phase was subsequently washed with water to remove residual alkaline components and then dried.

The purified pyrolysis distillate was subjected to fractional distillation in a laboratory rectification apparatus equipped with a packed column. The stabilized fraction collected

within the 160–180 °C boiling range was used as the C9 aromatic feedstock for the subsequent synthesis. GC–MS analysis of this fraction confirmed that it consisted predominantly of monoaromatic hydrocarbons, including alkyl-substituted benzene derivatives and other C9 aromatic compounds.

Synthesis of C9 aromatic alcohols

The isolated C9 aromatic fraction was subjected to a hydroxymethylation reaction with formaldehyde. A 39% aqueous formalin solution was used as the formaldehyde source. The molar ratio of aromatic compounds to formaldehyde was maintained at 1:1.

H-ZSM-5 zeolite was selected as the heterogeneous catalyst for the reaction. The catalyst was placed in a packed reactor, and the reaction mixture was brought into contact with the catalyst under heterogeneous conditions. The synthesis was carried out at 140–150 °C for 4 h. A reflux condenser was used to return volatile components to the reaction zone during the synthesis.

After completion of the reaction, the reaction mixture was cooled and filtered to remove residual catalyst. The resulting liquid product was collected for further characterization. Under the applied reaction conditions, the maximum product yield was reported to be 92%.

GC–MS analysis

The chemical composition of the synthesized product was determined by gas chromatography–mass spectrometry (GC–MS). The chromatographic analysis was used to identify the individual components of the obtained aromatic alcohol product and to estimate their relative abundances based on the corresponding chromatographic peak areas.

The identification of the detected compounds was performed by comparison of their mass spectra with spectral library data. The resulting chromatogram and identified components were used to evaluate the composition of the product obtained from the C9 aromatic feedstock.

FTIR characterization

Fourier-transform infrared (FTIR) spectroscopy was used to characterize the functional groups present in the synthesized product. The FTIR spectrum was compared with reference spectral data to identify the characteristic absorption bands associated with the aromatic framework and oxygen-containing functional groups.

Particular attention was paid to the absorption region characteristic of hydroxyl groups and to the characteristic vibrations of the aromatic ring. The FTIR results were used together with the GC–MS data to confirm the formation of aromatic alcohol-containing products during the reaction of the C9 aromatic fraction with formaldehyde.

RESULTS AND DISCUSSION

3.1. GC–MS analysis of the synthesized aromatic alcohols

The chemical composition of the aromatic alcohol product obtained from the C9 aromatic fraction was investigated using gas chromatography–mass spectrometry (GC–MS). The GC–MS chromatographic profile of the obtained product is presented in Figure 1 and table 1. The analysis was performed to characterize the composition of the synthesized

product and to identify the compounds formed during the reaction of the C9 aromatic fraction with formaldehyde in the presence of H-ZSM-5 catalyst.

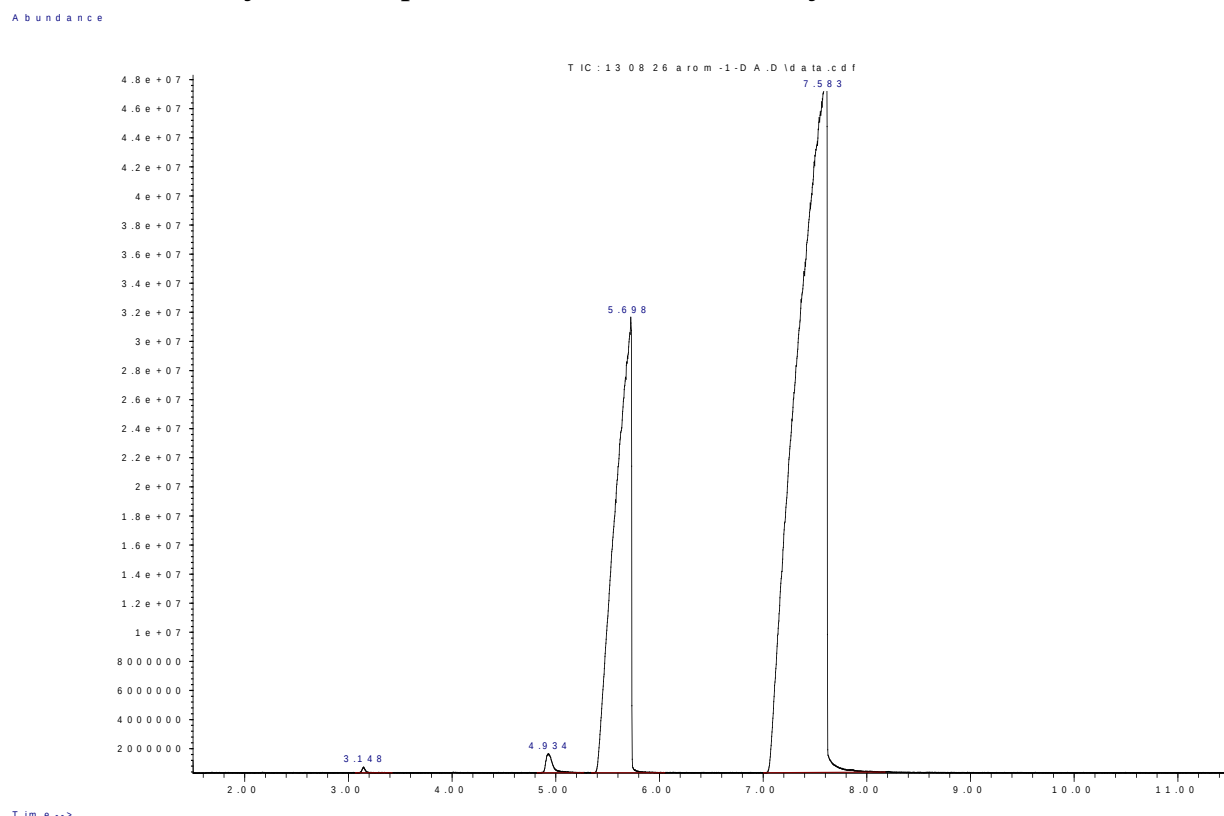


Figure 1. GC-MS chromatogram of the obtained aromatic alcohol product.

Table 1.

GC-MS analysis of the synthesized aromatic alcohol product

Peak No.	RT (min)	Area (%)	Compound identified by GC-MS	CAS No.	Qual.
1	3.148	0.07	Benzene, (1-methylethenyl)-	98-83-9	96
2	4.934	0.47	1-Phenyl-ethanone	98-86-2	94
3	5.698	26.30	Benzenemethanol, α,α -dimethyl-	617-94-7	91
4	7.583	73.16	1-Phenylpropanol-(1)	93-54-9	93

The GC-MS results indicate that the synthesized product predominantly consists of two aromatic alcohol components. The major component was 1-Phenylpropanol-(1), which accounted for 73.16 Area% of the total chromatographic area, with a library matching quality of 93%. The second major component was Benzenemethanol, α,α -dimethyl-, representing 26.30 Area% with a matching quality of 91%.

The combined relative abundance of these two aromatic alcohols reached 99.46 Area%, indicating that they constitute the predominant fraction of the synthesized product. In comparison, 1-Phenyl-ethanone and Benzene, (1-methylethenyl)- were detected only as minor components, accounting for 0.47 Area% and 0.07 Area%, respectively. Thus, their combined contribution was only 0.54 Area%.

The high relative abundance of the two aromatic alcohols demonstrates that the reaction of the C9 aromatic fraction with formaldehyde in the presence of H-ZSM-5 resulted predominantly in the formation of oxygen-containing aromatic products. Among the identified compounds, 1-Phenylpropanol-(1) was clearly the dominant product, with an approximately 2.8-fold higher relative abundance than Benzenemethanol, α,α -dimethyl-. The

GC-MS library matching values of 91-93% for the two major products provide strong spectral agreement for their identification.

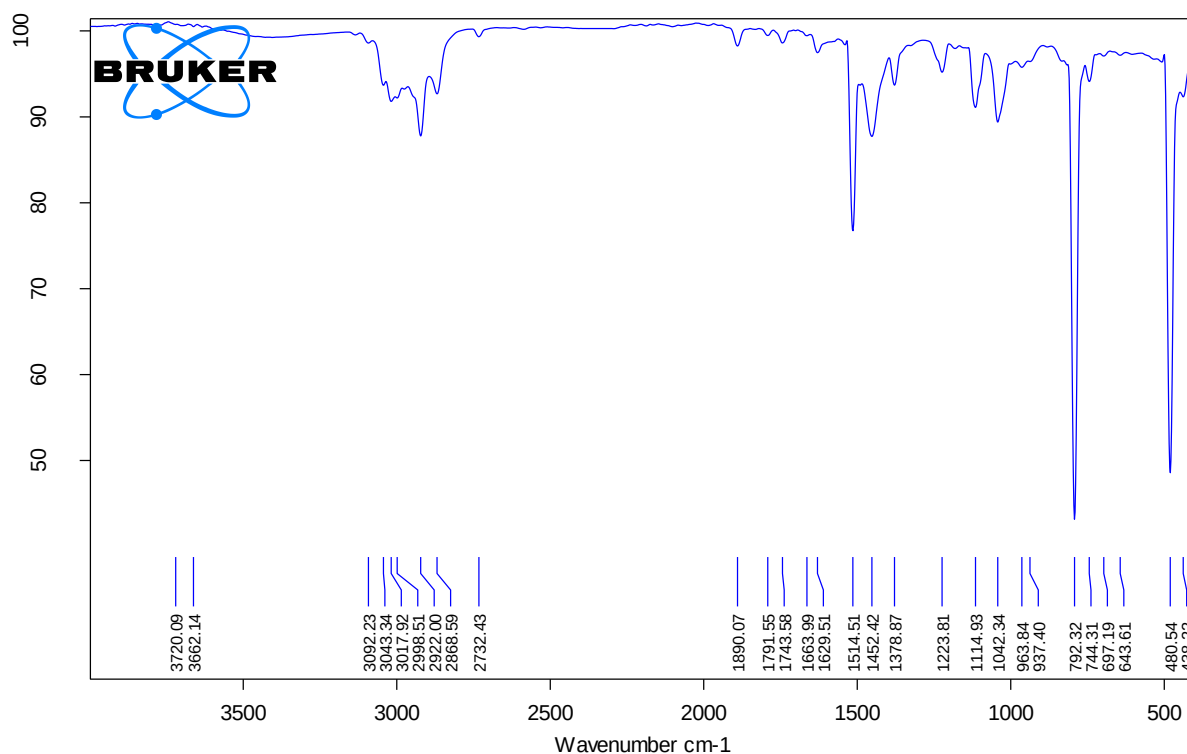


Figure 2. FTIR Characterization of the Synthesized Aromatic Alcohols

The FTIR spectrum of the synthesized aromatic alcohol product is presented in Figure 2. Several characteristic absorption bands associated with hydroxyl, aromatic, and aliphatic structural groups were observed, providing additional evidence for the formation of oxygen-containing aromatic compounds.

The absorption bands observed at 3720.09 and 3652.14 cm^{-1} are assigned to O-H stretching vibrations, indicating the presence of hydroxyl groups in the synthesized product. The bands at 3092.28 and 3047.36 cm^{-1} are characteristic of aromatic C-H stretching vibrations and confirm the presence of benzene-ring structures. A series of bands at 2993.80, 2969.51, 2928.89, and 2880.89 cm^{-1} can be attributed mainly to aliphatic C-H stretching vibrations of methyl- and methine-containing substituents attached to the aromatic structures.

The aromatic framework is further supported by the absorption bands in the 1684-1413 cm^{-1} region. In particular, the bands at 1629.91, 1454.51, 1412.41, and 1378.87 cm^{-1} are associated with aromatic skeletal and C-H deformation vibrations. The fingerprint region contains several characteristic absorptions, including bands at 1223.81, 1144.98, and 1093.84 cm^{-1} . These bands are particularly important because absorptions in this region are consistent with C-O stretching vibrations of alcohol groups.

Additional bands observed at approximately 963.40 and 937.40 cm^{-1} , together with the absorptions at 798, 744.31, 692.19, and 643.61 cm^{-1} , can be associated with C-H deformation and out-of-plane vibrations of substituted aromatic rings. The combination of the O-H stretching bands, aromatic C-H absorptions, and C-O stretching bands provides spectroscopic evidence for the presence of aromatic alcohol functionalities in the synthesized product.

Overall, the FTIR results are consistent with the GC–MS findings, which showed that the product was predominantly composed of 1-Phenylpropanol-(1) and Benzenemethanol, α,α -dimethyl-. Thus, the FTIR analysis provides complementary structural evidence for the formation of aromatic alcohol products from the C9 aromatic fraction through reaction with formaldehyde in the presence of H-ZSM-5 catalyst.

CONCLUSION

In this study, a C9 monoaromatic fraction obtained from pyrolysis distillate was successfully converted into aromatic alcohol-containing products through reaction with formaldehyde in the presence of H-ZSM-5 zeolite catalyst. The synthesis was carried out using 39% formalin at an aromatic compound-to-formaldehyde molar ratio of 1:1, at 140–150 °C for 4 h. Under these conditions, a maximum product yield of 92% was achieved.

GC–MS analysis demonstrated that the obtained product was predominantly composed of two aromatic alcohols: 1-Phenylpropanol-(1) with a relative peak area of 73.16% and Benzenemethanol, α,α -dimethyl- with 26.30%. Together, these two compounds accounted for 99.46% of the total chromatographic area, while the remaining identified components represented only 0.54%.

FTIR spectroscopy provided complementary evidence for the formation of aromatic alcohol functionalities. The observed O-H stretching bands in the 3700–3650 cm^{-1} region, together with characteristic aromatic C-H and C-O stretching absorptions, confirmed the presence of hydroxyl-containing aromatic structures in the synthesized product.

Overall, the combined GC-MS and FTIR results confirm that the C9 aromatic fraction of pyrolysis distillate can be effectively transformed into an aromatic alcohol-rich product using H-ZSM-5 as a heterogeneous catalyst. The obtained 92% yield and high proportion of the two identified aromatic alcohol components demonstrate the potential of this approach for the value-added utilization of pyrolysis-derived aromatic hydrocarbons.

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