Sang, Yushuai; Yang, Mingze; Agyingi, Cedric; Li, Yongdan

Pentaethylphenol (Not 2,6-di-tert-butyl-4-ethylphenol) verified as the primary product of guaiacol ethanol alkylation reaction

Published in:
Catalysis Today

DOI:
10.1016/j.cattod.2024.115081

Published: 01/02/2025

Document Version
Publisher's PDF, also known as Version of record

Catalysis Today 445 (2025) 115081

Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

Pentaethylphenol (Not 2,6-di-tert-butyl-4-ethylphenol) verified as the primary product of guaiacol ethanol alkylation reaction

Yushuai Sang [1], Mingze Yang [1], Cedric Agyingi, Yongdan Li [*]

Department of Chemical and Metallurgical Engineering, School of Chemical Engineering, Aalto University, Kemistintie 1, Espoo 16100, Finland

ARTICLE INFO

Keywords:
Lignin solvolysis
Guaiacol ethanol alkylation
Product identification
GC-MS
NMR

ABSTRACT

Guaiacol ethanol alkylation (GEA), a model reaction of lignin solvolysis, has been intensively investigated. However, the product identification with gas chromatograph-mass spectrometer (GC-MS) was wrong due to the defect of the GC-MS databases. In this work, the main product was isolated with a flash chromatography technique and analyzed with ^{1}H NMR and was identified as ethyl fully substituted phenol (or pentaethylphenol), which is contrary to the reported 2,6-di-tert-butyl-4-ethylphenol in previous literature. The NMR analysis of the entire product mixture further confirms that the product only contains ethyl substituted molecules, with no existence of isopropyl or tert-butyl substituted products. The byproducts, including ethyl partially substituted phenols, i.e., tetraethylphenol and triethylphenol, ethyl partially substituted guaiacol, 2-ethoxyphenol, and pentaethylbenzene, were also speculated based on the MS spectra. These findings rectify a long-standing error in product identification and may offer critical insights for mechanism investigations.

1. Introduction

Lignin, a key component of lignocellulose, is a huge amount renewable resource of aromatic compounds [1]. Recently, lignin solvolysis has emerged as a promising method for producing high-value small molecules [2]. Low-carbon alcohols, particularly ethanol, show promising reactivity in lignin solvolysis, achieving complete liquefaction and high monomer yields in several published works [3–8]. Guaiacol ethanol alkylation (GEA) has been intensively investigated as a representative model reaction of the alkylation steps in lignin ethanolysis and showed a notable potential in upgrading lignin-derived aromatics to biofuel [9].

Gas chromatograph-mass spectrometer (GC-MS) has been applied to identify the product distribution in lignin ethanolysis and GEA over a decade. In 2010, Tang et al. [10] investigated the catalytic hydrocracking of pyrolytic lignin-oil and reported isopropyl and tert-butyl substituted phenols as products using a Thermo Trace DSQ (I) GC-MS. Cheng et al. [11] in 2012 stated the formation of isopropyl and tert-butyl substituted phenols in the ethanolysis of alkali lignin, utilizing Shimazu QP2010S GC-MS. Huang et al. [6–8] in 2014 stated the formation of isopropyl substituted phenols in the ethanolysis of soda lignin, using Shimadzu 2010 GC-MS with NIST11 and NIST11s MS databases. In our previous work, Ma et al. [5] reported the existence of isopropyl-substituted products in the ethanolysis of Kraft lignin in 2015. In enzymatic hydrolysis lignin ethanolysis, isopropyl and tert-butyl substituted phenols were presented in the products in 2019 [12–14]. In our work done in Tianjin, China, Agilent 6890–5973 GC-MS with NIST02 MS database was employed. In 2021–2022, Chen et al. [15–17] investigated kraft lignin depolymerization to fuel and phenols and reported that isopropyl and tert-butyl substituted phenols as products with Thermo Scientific ISQ 7000 MS detector. Dou et al. [18] recorded the formation of isopropyl and tert-butyl substituted phenols in the hydrodeoxygenation of kraft lignin using an Agilent 7890 A GC/5975 C MS. Recently, Sang et al. [19] reported the isopropyl and tert-butyl substituted phenols in the product of enzymatic hydrolysis lignin ethanolysis.

Cui et al. [20] in 2017 stated that the primary products of GEA were isopropyl and tert-butyl substituted phenols with MoO_3 as a catalyst. Mai et al. [21] in 2019 marked the major products as isopropyl and tert-butyl substituted phenols in H_2WO_4 catalyzed GEA. In 2020, Yan et al. [22] reported the formation of isopropyl and tert-butyl substituted phenols in the Re_2O_7-catalyzed GEA. These mentioned works used an Agilent 6890–5973 GC-MS with NIST02 MS database. Most recently, Valizadeh et al. [23] in 2024 investigated $MoNi/CeO_2$ catalyzed GEA

* Corresponding author.
E-mail address: yongdan.li@aalto.fi (Y. Li).
[1] These authors are co-first authors and contributed equally.

https://doi.org/10.1016/j.cattod.2024.115081
Received 8 June 2024; Received in revised form 8 September 2024; Accepted 25 September 2024
Available online 26 September 2024

reaction and proposed isopropyl and tert-butyl substituted phenols as main products, using Agilent 7820A-5977E GC-MS with NIST MS database.

Despite different versions of GC-MS equipment and MS databases being used, consistent products, i.e., isopropyl and tert-butyl substituted phenols, were reported across various research groups. However, GC-MS relies on comparing the mass spectra of compounds in samples with those stored in its MS database for molecular identification. If the data of a molecule does not exist or the differences of the MS data of two or more molecules are minor in the MS database, the software may give a structure with similar MS spectra in the database, which leads to an erroneous product identification.

In this work, we combined GC-MS, product isolation, and nuclear magnetic resonance (NMR) techniques to identify the products in the GEA catalytic reaction. The main product was isolated and analyzed with ^{1}H NMR, while other byproducts were speculated according to their MS spectra. The entire product mixture was analyzed with the Heteronuclear Single Quantum Coherence-NMR(HSQC NMR). The comprehensive results confirm the presence of ethyl-substituted products, without any information of the isopropyl and tert-butyl substituted phenols, suggested by GC-MS database and reported in previous literature. With this work, we propose to correct the erroneous product identification that has been repeatedly reported for over a decade.

2. Methods and materials

2.1. Materials

Guaiacol, deuterated chloroform ($CDCl_3$) and ammonium meta tungstate hydrate were purchased from the Sigma-Aldrich company. 2,6-di-tert-butyl-4-ethylphenol (DTBEP) was purchased from TCI Europe. The hydrogen type zeolite Y (HY) and solvents, including ethanol, dodecane, n-hexane, and ethyl acetate, were purchased from Thermo scientific. WO_3/HY catalyst was prepared with an impregnation method, following the procedure outlined in our previous work [12].

2.2. Guaiacol alkylation

The GEA reaction was carried out in a 100 mL batch reactor (Kemi Co. Ltd, Hastelloy). In a typical reaction setup, 1 g of guaiacol, 0.2 g of WO_3/HY catalyst, and 50 mL of ethanol solvent were added into the reactor. After sealing and purging with pure N_2, the reactor was heated to 280 °C and kept for 4 h with a fixed stirring rate of 600 rpm. After the reaction, the mixture was filtrated to remove the catalyst.

2.3. Product analysis

HSQC NMR spectrum of the product was recorded using a Bruker AVANCE III HD 400 MHz instrument. After solvent removal at 40 °C under vacuum, the product (50 mg) was dissolved in $CDCl_3$ (0.6 mL) as the deuterated NMR solvent. Purification of the product was achieved through flash chromatograph, employing a silica gel column (VWR Silica gel 60) with a pore size of 40–63 μm and a hexane: ethyl acetate ratio of 10:1 for elution. Subsequently, the purified product (5 mg) was dissolved in $CDCl_3$ (0.6 mL), and its ^{1}H NMR spectrum was measured using the same HSQC NMR instrument.

GC-MS spectrum of the product was acquired using a Shimadzu GC equipped with MS detector, while quantitative analysis was achieved using an Agilent 7890 gas chromatograph equipped with a flame ionization detector (GC-FID). The conditions for both GC instruments were consistent with those used in our previous work [24].

3. Results

The GC-FID spectra of products obtained from GEA with WO_3/HY and MoO_3 are depicted in Fig. 1. Compared to MoO_3 used in previous work [20], WO_3/HY exhibits enhanced selectivity for the main product (product 7, P7), which is still reported as DTBEP with the GC-MS database for both product samples. Previous works on guaiacol alkylation in ethanol or methanol have also reported the formation of DTBEP [17,20–23]. To confirm the analysis result, a standard sample was analyzed using the same GC-FID. The retention time of the standard sample DTBEP differs greatly from that of P7, suggesting that P7 is not DTBEP. The MS spectra of P7 measured with Shimazu GC-MS-QP2010SE at our lab and DTBEP in the databases were compared in Fig. 2. P7 exhibited two strong fragment peaks at 219 and 234 and two moderate fragment peaks at 145 and 205. DTBEP exhibited also similar main fragment peaks at 219 and 234 but only one moderate fragment peak at 57. Moreover, the noticeably different Fourier-transform infrared spectroscopy (FTIR) spectra confirmed that P7 had a different structure from DTBEP (Figure S1).

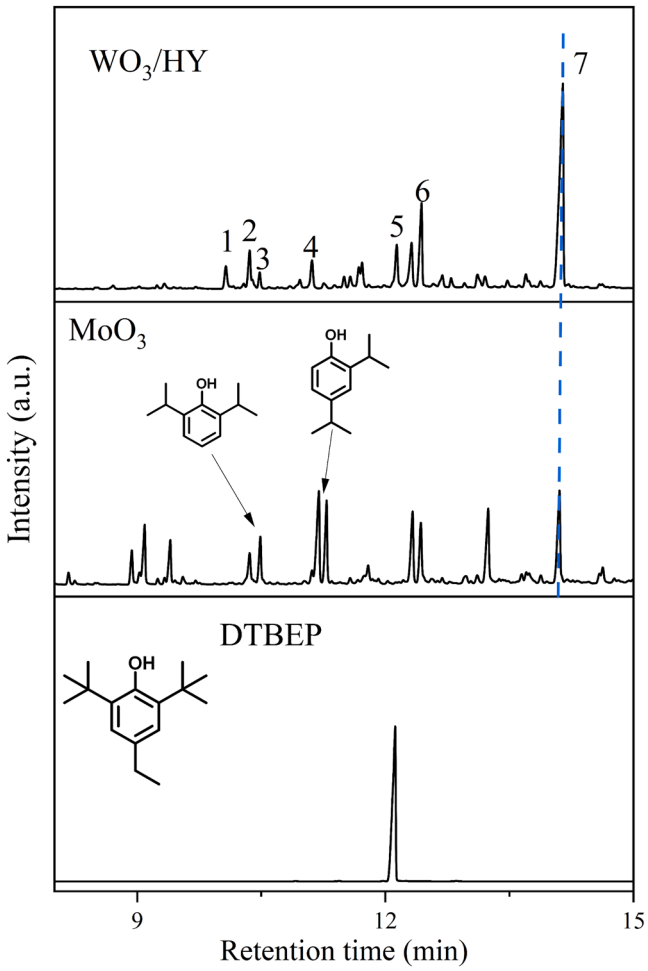

Fig. 1. The GC-FID spectra of the products of the GEA reaction catalyzed with WO_3/HY and MoO_3 and the standard sample of DTBEP. (Reaction conditions: 1 g guaiacol, 0.2 g catalyst, 50 mL ethanol, 280 °C, 0 MPa N_2, 4 h).

Due to the high peak area of P7 in the GC spectrum, a flash chromatograph was employed to isolate the molecule. The ^{1}H NMR spectra of DTBEP and P7 are compared in Fig. 3. In the spectrum of DTBEP, five distinct peaks are discernible. The sharp singular peak at 1.45 ppm corresponds to the hydrogen atoms in the tert-butyl group, whereas the multiple peaks at 1.23 ppm and 2.59 ppm arise from the hydrogen atoms in the methyl and methylene of the ethyl group, respectively. The active H atom in the phenolic hydroxyl group contributes to the singular peak at 5.03 ppm [25]. The singular peak at 7.01 ppm corresponds to the hydrogen atoms attached to the benzene ring. In the spectrum of the P7 sample, the multiple peaks corresponding to the hydrogen atoms in

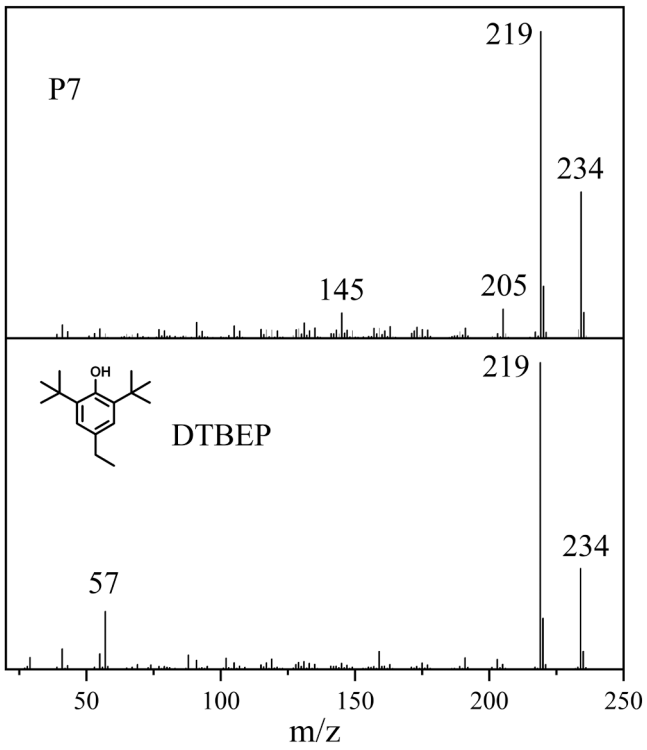

Fig. 2. The MS spectra of P7 and DTBEP in the MS library.

the methyl and methylene of the ethyl group are also observed in the spectrum of P7 sample. The methyl and methylene peaks appear at 1.17 ppm and 2.64 ppm with a 15:10 peak area ratio. The single peak at 4.56 ppm is ascribed to the hydrogen atom in the hydroxyl group [26]. The absence of signals corresponding to hydrogen atoms on the benzene ring indicates the complete substitution of hydrogen atoms. Other small peaks are derived from the impurities with a concentration below 10 %. The P7 sample was further analyzed using ^{13}C NMR, and the ^{13}C NMR spectrum (Figure S2) was consistent with the ^{1}H NMR spectrum.

HSQC NMR was applied to analyze the entire product mixture obtained after the reaction and solvent evaporation. As shown in Fig. 4, strong signals were observed at δC/δH = 9–20 ppm/0.7–1.3 ppm and δC/δH = 13–30 ppm/2.1–2.6 ppm, corresponding to the C-H cross signal of -CH_3 and -CH_2- groups in ethyl groups, respectively [27]. Meanwhile, weak signals attributed to the C-H cross signal of methoxy and ethoxy groups were observed at δC/δH = 55 ppm/3.7 ppm and 65 ppm/3.9 ppm, respectively [27]. Noticeably, no signals corresponding to -CH3 in tert-butyl groups (δC/δH = 30 ppm/1.45 ppm) or -CH- in isopropyl groups (δC/δH = 27–30 ppm/3–3.3 ppm) were observed [28,29]. The HSQC NMR analysis confirms that the products only contain ethyl groups without isopropyl or tert-butyl groups.

The MS analysis reveals the maximum values of *m/z* (Max. *m/z*) for Products 1–7 (P1-P7). Among them, P7 exhibits the highest Max. *m/z* of 234, while the Max. *m/z* of P2 and P6 are 178 and 206, respectively, which differ by multiples of 28 from that of P7. P1 and P4 both exhibit a Max. *m/z* of 194, while P3 shows a Max. *m/z* of 180, and P5 exhibits a Max. *m/z* of 218. Further analysis of the MS spectra of ethyl catechol, 2-ethoxyphenol, P1, and P4 (Fig. 5) reveals the main fragment peaks. Ethyl catechol displays main fragment peaks at 123 and 138, while 2-ethoxyphenol exhibits main fragment peaks at 110 and 138. In contrast, the MS spectrum of P1 shows three main fragment peaks at 151, 166, and 194, while that of P4 has four main fragment peaks at 151, 166, 179, and 194.

4. Discussion

4.1. Product identification

The GC-FID results difference between the products of GEA and the standard sample indicates the product identification based on GC-MS is wrong. The P7 sample was isolated with a flash chromatograph. The noticeable different FTIR spectra also indicate the different structure of DTBEP and P7 (Figure S1). In the results of analyzing the P7 sample and standard sample with ^{1}H NMR, the absence of the tert-butyl signal in the P7 sample confirms that P7 is not DTBEP. In the spectrum of the P7 sample, the main signals are methyl and methylene in the ethyl groups, and a signal from hydrogen in the hydroxyl group remains. That means the P7 should be a phenolic compound with multiple ethyl groups. The absence of the benzene-ring hydrogen signal indicates the full substitution of the benzene ring. Therefore, P7 is pentaethylphenol which has a consistent Max. *m/z* of 234 provided by GC-MS, which equals to the molecular weight of both DTBEP and pentaethylphenol. The structure of P7 is also confirmed as pentaethylphenol based on ^{13}C NMR (Figure S2).

The GC-MS analysis suggested the molecular structures of P2 and P6 as 2,6-di-isopropylphenol and 2,6-di-tert-butylphenol, respectively, while failed to provide reasonable structures for P1, P3, P4, and P5. However, HSQC NMR results indicate that the products of GEA are mainly ethyl substituted compounds and exclude the existence of the isopropyl group and tert-butyl group in the product. Therefore, the identifications of P1-P6 are also unreliable in previous literature [20–23]. Due to the low concentrations of these products, their separation was challenging. The corresponding molecular structures of P1-P6 are speculated based on their MS spectra and HSQC NMR results. The Max. *m/z* of the molecules corresponding to P2 and P6 exhibit multiple 28 differences from the Max. *m/z* of P7 (234). Therefore, P2 and P6 might reflect the molecules having similar structures with P7 but with different numbers of ethyl groups. Based on their Max. *m/z*, P2 and P6 are speculated as triethylphenol and tetraethylphenol, respectively. The Max. *m/z* of P1 and P4 are the same, i.e., 194, which is 16 greater than that of P2, indicating the presence of an additional oxygen atom in the molecule of P1 and P4 compared to that of P2. Therefore, P1 and P4 could be the alkylated derivatives of 2-ethoxyphenol or ethyl catechol. We found that 2-ethoxyphenol demonstrates a 28 difference between its first main fragment peak and the second main fragment peak, while for ethylcatechol, this difference is 15 (Fig. 5). Therefore, we infer that 2-ethoxyphenol tends to first lose the ethyl group of the ethoxy moiety during ionization, whereas ethyl catechol first loses the methyl group of the ethyl on the benzene ring. Based on this rule and the MS spectra of P1 and P4, we speculate P1 as 2-ethoxy-diethylphenol and P4 as triethyl catechol. Similarly, P3 is proposed to be diethyl guaiacol. Interestingly, P5 exhibits a maximum *m/z* value of 218, 16 lower than that of P7, indicating one less oxygen atom compared to P7. Hence, P5 is likely pentaethylbenzene.

Herein, we clarify that the products obtained from GEA, as depicted in Fig. 6. Unlike the isopropyl and tert-butyl alkylated products recorded via only CC-MS, our analysis reveals that the main products are ethyl-alkylated phenols. The primary product is pentaethylphenol (P7). The other two significant products are very likely tetraethylphenol (P6) and triethylphenol (P2). The small amounts of byproducts are assumed to include: 2-ethoxy-diethylphenol (P1), diethyl guaiacol (P3), and triethyl catechol (P4), which have two oxygen-containing functional groups, and a product without oxygen-containing functional groups, i.e., pentaethylbenzene (P5).

4.2. Limitation of the identification methods

The capacity of GC-MS to detect multiple compounds within intricate samples has made it a crucial tool in molecular qualitative analysis, which relies on comparing the mass spectra of the compounds with those stored in its database. However, when a specific molecular structure is

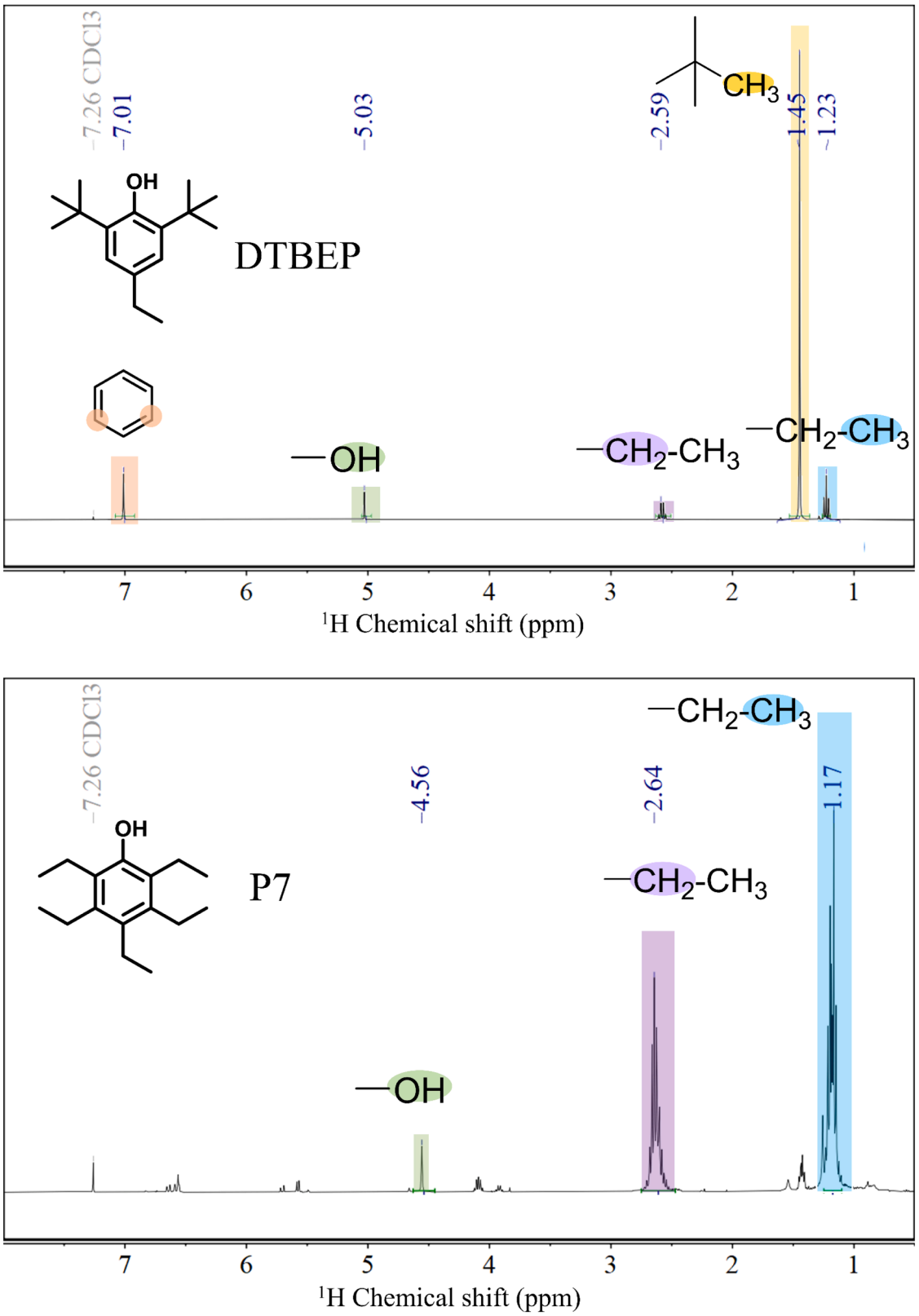

Fig. 3. ^{1}H NMR spectra of DTBEP and the sample of P7.

absent or its MS spectrum is close to that of another molecule in the database, accurate identification becomes challenging [30]. NMR spectroscopy offers direct insights into atomic connectivity and molecular environments, making it highly effective for determining organic molecular structures, especially for those first synthesized and not yet present molecules in GC-MS databases. Nevertheless, NMR analysis requires high sample purity, rendering it unsuitable for complex mixtures. The intricate structure of lignin and the complexity of the reaction mechanism inevitably result in the formation of complex products during lignin solvolysis. Although GC-MS has been commonly used for

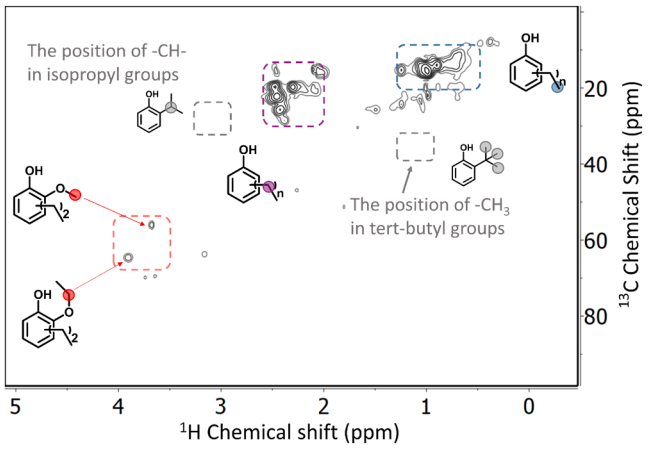

Fig. 4. The HSQC NMR spectrum of the whole mixture obtained after the reaction with solvent evaporation.

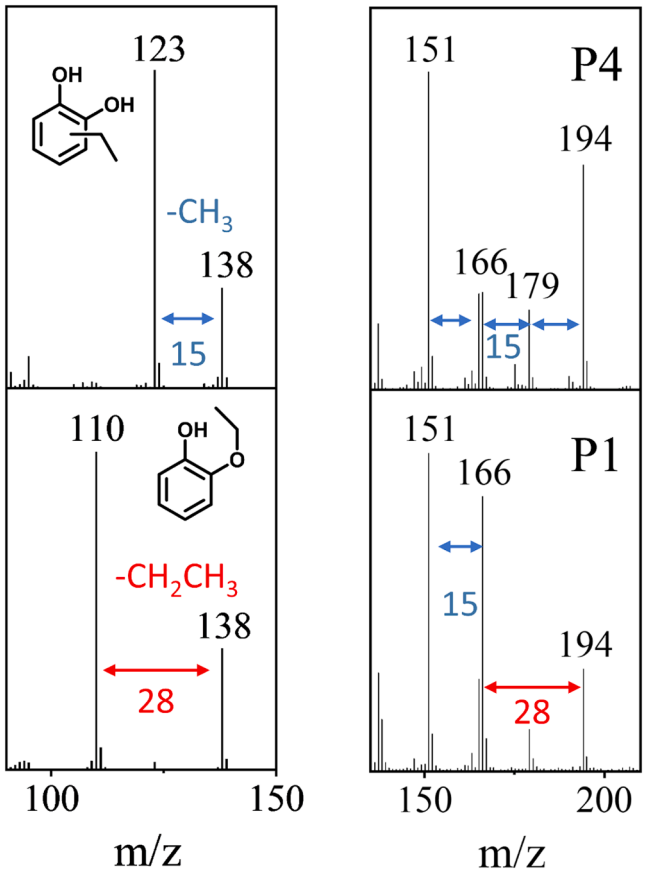

Fig. 5. MS spectra of ethyl catechol, 2-ethoxyphenol, P1, and P4.

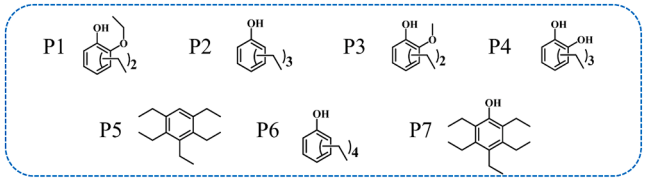

Fig. 6. Structures of P1-P7.

product identification in doing lignin solvolysis, our findings here raise doubts about its results.

In lignin ethanolysis, isopropyl and tert-butyl alkylated phenols are regarded as the products of the alkylation reaction between phenolic monomers and ethanol solvent. Similar product distributions have been observed in GEA, serving as a model reaction. However, in this work, the ^{1}H NMR analysis of P7 confirmed the main product is pentaethylphenol, not DTBEP. Comparing the MS spectra of pentaethylphenol and DTBEP, we found that they exhibit the same main fragment peaks at 219 and 234 but have major differences in the other fragment peaks with comparatively small amounts. Pentaethylphenol is scarcely documented in previous literature, unavailable commercially, and not listed in any MS database. This is the first time that pentaethylphenol was reported with its MS and ^{1}H NMR spectra. Therefore, the GC-MS databases failed to provide a correct molecular structure.

The identification of the byproducts, especially P2 which was reported as isopropyl substituted phenol with the database now we use, and the other four products in MoO_3 catalyzed GEA (Fig. 1.) are also questionable based on the HSQC NMR results. However, their low selectivity makes their separation challenging, and we can only speculate their structures based on their MS spectra. Designing a catalyst with high selectivity toward isopropyl substituted phenols would enable better separation, allowing for the verification of the structures of these products.

These findings highlight the limitations of relying solely on GC-MS for product identification in lignin solvolysis and lignin model compound reactions. To ensure correct product identification, a methodology combining GC-MS with NMR techniques should be developed.

5. Conclusion

GC-MS and NMR techniques were combined for product identification of GEA reaction, correcting the long-standing incorrect identification of the main product as DTBEP. The main product of GEA reaction was isolated and analyzed with ^{1}H NMR and was identified as pentaethylphenol according to its ^{1}H NMR spectrum. HSQC NMR analysis of the entire product mixture confirmed the presence of ethyl-substituted products, with no information of isopropyl or tert-butyl substituted products as reported in previous literature works. The by-products, including tetraethylphenol, triethylphenol, 2-ethoxy-diethylphenol, diethyl guaiacol, triethyl catechol, and pentaethylbenzene, are speculated to exist based on their MS spectra. These different product structures highlight the limitation of GC-MS when identifying new compounds not existing in the databases. A more reliable and standardized method for identifying product structures like the combination of GC-MS and NMR should be developed, and the structure of isopropyl-substituted products also needs to be double-checked when separation is possible.

CRediT authorship contribution statement

Cedric Agyingi: Investigation, Data curation. **Yushuai Sang:** Investigation, Formal analysis, Data curation, Conceptualization. **Mingze Yang:** Writing – original draft, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Yongdan Li:** Writing – review & editing, Supervision.

Declaration of Competing Interest

None

Data availability

Data will be made available on request.

Acknowledgment

This work has received funding from the European Union's Horizon 2020 research and innovation program, (BUILDING A LOW-CARBON, CLIMATE RESILIENT FUTURE: SECURE, CLEAN AND EFFICIENT ENERGY) under Grant Agreement No 101 006 744. The content presented in this document represents the views of the authors, and the European Commission has no liability in respect of the content.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.cattod.2024.115081.

References

[1] C. Li, X. Zhao, A. Wang, G.W. Huber, T. Zhang, Catalytic transformation of lignin for the production of chemicals and fuels, Chem. Rev. 115 (2015) 11559–11624.
[2] Z. Sun, B. Fridrich, A. de Santi, S. Elangovan, K. Barta, Bright side of lignin depolymerization: toward new platform chemicals, Chem. Rev. 118 (2018) 614–678.
[3] Y. Sang, H. Chen, M. Khalifeh, Y. Li, Catalysis and chemistry of lignin depolymerization in alcohol solvents - a review, Catal. Today 408 (2023) 168–181.
[4] A.C. Garcia, S. Cheng, J.S. Cross, Solvolysis of kraft lignin to bio-oil: a critical review, Clean. Technol. 2 (2020) 513–528.
[5] X. Ma, R. Ma, W. Hao, M. Chen, F. Yan, K. Cui, Y. Tian, Y. Li, Common pathways in ethanolysis of kraft lignin to platform chemicals over molybdenum-based catalysts, ACS Catal. 5 (2015) 4803–4813.
[6] X. Huang, C. Atay, T.I. Korányi, M.D. Boot, E.J.M. Hensen, Role of Cu–Mg–Al mixed oxide catalysts in lignin depolymerization in supercritical ethanol, ACS Catal. 5 (2015) 7359–7370.
[7] X. Huang, T.I. Korányi, M.D. Boot, E.J.M. Hensen, Ethanol as capping agent and formaldehyde scavenger for efficient depolymerization of lignin to aromatics, Green. Chem. 17 (2015) 4941–4950.
[8] X. Huang, T.I. Korányi, M.D. Boot, E.J.M. Hensen, Catalytic depolymerization of lignin in supercritical ethanol, ChemSusChem 7 (2014) 2276–2288.
[9] G. De Smet, X. Bai, B.U.W. Maes, Selective C(aryl)–O bond cleavage in biorenewable phenolics, Chem. Soc. Rev. (2024).
[10] Z. Tang, Y. Zhang, Q. Guo, Catalytic hydrocracking of pyrolytic lignin to liquid fuel in supercritical ethanol, Ind. Eng. Chem. Res. 49 (2010) 2040–2046.
[11] S. Cheng, C. Wilks, Z. Yuan, M. Leitch, C. Xu, Hydrothermal degradation of alkali lignin to bio-phenolic compounds in sub/supercritical ethanol and water–ethanol co-solvent, Polym. Degrad. Stab. 97 (2012) 839–848.
[12] F. Mai, Z. Wen, Y. Bai, Z. Ma, K. Cui, K. Wu, F. Yan, H. Chen, Y. Li, Selective Conversion of enzymatic hydrolysis lignin into alkylphenols in supercritical ethanol over a WO3/γ-Al2O3 catalyst, Ind. Eng. Chem. Res. 58 (2019) 10255–10263.
[13] Y. Bai, K. Cui, Y. Sang, K. Wu, F. Yan, F. Mai, Z. Ma, Z. Wen, H. Chen, M. Chen, Y. Li, Catalytic depolymerization of a lignin-rich corncob residue into aromatics in supercritical ethanol over an alumina-supported NiMo alloy catalyst, Energy Fuels 33 (2019) 8657–8665.
[14] K. Wu, Y. Sang, S. Kasipandi, Y. Ma, H. Jiao, Q. Liu, H. Chen, Y. Li, Catalytic roles of Mo-based sites on MoS2 for ethanolysis of enzymatic hydrolysis lignin into aromatic monomers, Catal. Today 408 (2023) 211–222.
[15] C. Li, J. Shi, K. Zhang, Y. Wang, Z. Tang, M. Chen, Efficient conversion of Kraft lignin to guaiacol and 4-alkyl guaiacols over Fe-Fe3C/C based catalyst under supercritical ethanol, Fuel 315 (2022) 123249.
[16] M. Chen, Z. Tang, Y. Wang, J. Shi, C. Li, Z. Yang, J. Wang, Catalytic depolymerization of Kraft lignin to liquid fuels and guaiacol over phosphorus modified Mo/Sepiolite catalyst, Chem. Eng. J. 427 (2022) 131761.
[17] M. Chen, J. Zhang, Y. Wang, Z. Tang, J. Shi, C. Wang, Z. Yang, J. Wang, H. Zhang, Lignin catalytic depolymerization for liquid fuel and phenols by using Mo/sepiolite catalysts calcined at different temperature, J. Environ. Chem. Eng. 9 (2021) 105348.
[18] X. Dou, W. Li, C. Zhu, X. Jiang, Catalytic waste Kraft lignin hydrodeoxygenation to liquid fuels over a hollow Ni-Fe catalyst, Appl. Catal., B 287 (2021) 119975.
[19] Y. Sang, M. Yang, H. Chen, Y. Li, Ethanolysis of enzymatic hydrolysis lignin with Ni catalysts on different supports: The roles of catalytic sites, Catal. Today 438 (2024) 114750.
[20] K. Cui, L. Yang, Z. Ma, F. Yan, K. Wu, Y. Sang, H. Chen, Y. Li, Selective conversion of guaiacol to substituted alkylphenols in supercritical ethanol over MoO3, Appl. Catal., B 219 (2017) 592–602.
[21] F. Mai, K. Cui, Z. Wen, K. Wu, F. Yan, M. Chen, H. Chen, Y. Li, Highly selective conversion of guaiacol to tert-butylphenols in supercritical ethanol over a H 2 WO 4 catalyst, RSC Adv. 9 (2019) 2764–2771.
[22] F. Yan, Y. Sang, Y. Bai, K. Wu, K. Cui, Z. Wen, F. Mai, Z. Ma, L. Yu, H. Chen, Y. Li, Guaiacol demethoxylation catalyzed by Re2O7 in ethanol, Catal. Today 355 (2020) 231–237.
[23] S. Valizadeh, Y. Khani, B.S. Kang, J. Hwang, J. Jae, C.H. Ko, J.W. Han, Y.-K. Park, Catalytic conversion of guaiacol to phenol and alkylphenols over Mo-promoted Ni/CeO2 catalyst in supercritical ethanol, Appl. Catal. B: Environ. Energy 348 (2024) 123823.
[24] Y. Sang, Y. Ma, G. Li, K. Cui, M. Yang, H. Chen, Y. Li, Enzymatic hydrolysis lignin dissolution and low-temperature solvolysis in ethylene glycol, Chem. Eng. J. 463 (2023) 142256.
[25] S. Ng, Nuclear magnetic resonance spectra of adamantyl-substituted phenols and solvent-induced shifts of sterically hindered protons, J. Chem. Soc., Perkin Trans. 2 (1972) 1514–1517.
[26] F. Alonso, M. Yus, Easy synthesis of 2,4-dialkyl substituted phenols and anisoles from p-bensoquinone, Tetrahedron 48 (1992) 2709–2714.
[27] Y. Sang, K. Wu, Q. Liu, Y. Bai, H. Chen, Y. Li, Catalytic ethanolysis of enzymatic hydrolysis lignin over an unsupported nickel catalyst: the effect of reaction conditions, Energy Fuels 35 (2021) 519–528.
[28] R. Rusew, K. Iliev, V. Kurteva, B. Shivachev, 1-(2-(3,5-Di-tert-butyl-4-hydroxyphenyl)-2-oxoethyl) quinolin-1-ium bromide, Molbank 2024 (2024) M1763.
[29] L. Vinet, L. Di Marco, V. Kairouz, A.B. Charette, Process intensive synthesis of propofol enabled by continuous flow chemistry, Org. Process Res. Dev. 26 (2022) 2330–2336.
[30] F.W. McLafferty, D.A. Stauffer, S.Y. Loh, C. Wesdemiotis, Unknown identification using reference mass spectra. quality evaluation of databases, J. Am. Soc. Mass Spectrom. 10 (1999) 1229–1240.