

Solid Acid Catalytic (Fe³⁺/TiO₂) Transformation of Alkaline Lignin into Aromatic Compounds



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Abstract: Lignocellulosic biomass is composed of lignin, hemicellulose, and cellulose. Due to its intricate molecular structure, lignin is largely underutilized, whereas the conversion of cellulose and hemicellulose has been extensively studied in recent years. Lignin is often combusted as waste, which poses environmental challenges and drives the need for research into its valorization. This study focus on the optimization of the valorization of alkaline lignin into aromatic compounds in a one-pot process using Fe³⁺/TiO₂ as a solid acid catalyst. A central composite design (CCD) was employed to optimize the process parameters (temperature (200-213 °C), catalyst loading (4.6-11 g of Fe³⁺/TiO₂), and reaction time (46-113 minutes)) for the depolymerization of 10 g of commercial alkaline lignin into aromatic compounds. The optimal depolymerization conditions achieved a 47.93% yield of aromatics as identified by GCMS, were determined at 206 °C, 4.51 g of Fe³⁺/TiO₂ catalyst, and a reaction time of 86 minutes. Characterization of the commercial alkaline lignin was done using Fouriertransform infrared spectroscopy (FTIR), Walkley and Black method, flame photometry, atomic absorption spectrometry and wet digestion method. FTIR analysis confirmed that the commercial alkaline lignin contained hydroxyl functional groups at the band of 3276.3 cm⁻¹. Elemental analysis using the Walkley-Black method, flame photometry, atomic absorption spectrometry, and wet digestion revealed the carbon, sodium, sulfur, and nitrogen contents of the lignin as 50.00%, 13.35%, 5.22%, and 0.65%, respectively. The melting point, bulk density, moisture content, and ash content of the lignin were determined to be 200 °C, 0.5124 g/cm³, 3.57% and 22.74%, respectively. The XRD pattern indicated the presence of titanium oxide and iron oxide. The XRD analysis also displayed several sharp peaks, indicative of the catalyst's crystalline nature. Lignocellulosic Biomass, Depolymerization, Aromatics and Alkaline Lignin. Keywords:

Introduction

Non-renewable energy resources, particularly fossil feedstocks such as crude oil, coal, and natural gas, are derived from the remains of dead organisms subjected to high pressures and temperatures over geological time scales (Cong, 2022). These feedstocks are critical for meeting the global demand for energy, chemicals, and materials (Cong, 2022). According to data from the world energy research in the U.S. Energy Information Administration (2007), the primary energy sources include natural gas (23.0%), crude oil (36.0%), and coal (27.4%), which collectively account for 86.4% of the total energy supply (Looney, 2021). The remaining energy sources include nuclear (8.5%), hydroelectric (6.3%), and other renewables such as geothermal, waste, tidal, wind, and solar (0.9%) (Looney, 2021). Notably, approximately 96% of the energy used in the transportation sector is derived from fossil feedstocks, primarily crude oil (Hess, et al., 2011; Ribeiro et al., 2007). Global energy consumption is projected to increase at an annual rate of 2.3% (Paresh & Dhepe, 2014).

Fossil feedstocks enable the production of a wide array of fuels and chemicals (Spliethoff, 2010). Coal, used as a solid fuel, is primarily combusted to generate electricity and heat (Spliethoff, 2010). The Fischer-Tropsch process facilitates the conversion of coal into carbon monoxide (CO) and hydrogen (H₂), which can then be synthesized into transportation fuels like gasoline and diesel (Andrews & Division, 2008; Mesfun, 2022). Crude oil, a key component of fossil feedstocks, is processed in petrochemical refineries to produce products such as liquefied petroleum gas (LPG), gasoline, asphalt, naphtha, kerosene, and heating oil (Paresh & Dhepe, 2014). Crude oil also yields various hydrocarbons, including paraffins, aromatics, naphthenes, alkenes, and alkynes (Paresh & Dhepe, 2014). Natural gas, predominantly composed of methane (70-90%), along with minor constituents like nitrogen (0-5%), hydrogen sulfide (0-5%), and carbon dioxide (0-8%), is another significant hydrocarbon source (Paresh & Dhepe, 2014).

The advantages of fossil feedstocks include their availability and capacity to generate substantial quantities of fuels, chemicals, and energy. However, the rapid consumption of these resources, driven by population growth, poses significant challenges (Mccarthy, 2021). For instance, Nigeria's annual crude oil reserved in 2023 decreased by 0.46 % when compared with 2022 which stood at 36.096 billion barrels (NUPRC Annual Report, 2023). Similarly, Nigeria produced around 2.503 TCF (trillion cubic feet) of natural gas in 2023 which reflect a decrease of 0.57 % compared to year 2022 (NUPRC Annual Report, 2023). The increasing demand for fossil feedstocks highlights the urgent need to address their disadvantages (Amin, 2018). These include finite reserves, escalating consumption rates, and the potential for depletion in the near future (Mccarthy, 2021). Additionally, the combustion of fossil feedstocks contributes significantly to global warming and climate change due to the release of carbon dioxide (CO₂). It is estimated that 21.3 billion tonnes of CO2 are emitted annually from fossil fuel consumption, yet photosynthetic processes can only absorb approximately 10.65 billion tonnes of CO₂, exacerbating atmospheric CO₂ levels (Kalak, 2023; Matthew et al., 1998; Prasad, 2014). Furthermore, the uneven geographical distribution of fossil feedstock reserves contributes to economic, security, and political tensions worldwide (Paresh & Dhepe, 2014).

Given the challenges associated with fossil feedstocks, there is a growing need to transition to renewable energy resources, which are abundantly available and can mitigate these issues, including the impact of global warming (Matthew *et al.*, 1998). There is a gradual shift from fossil feedstocks to renewable energy sources (Mccarthy, 2021). The United States (US) and the European Union (EU) have set ambitious targets to derive 25% of chemicals and 20% of fuel from renewable resources by 2030 (Amin, 2018; Mccarthy, 2021).

Moreover, previous research has explored various solid acid catalysts, like Pt/TiO₂ catalysts (Cabral *et al.*, 2021) and, ZSM-5-incorporated metal catalysts (Xia *et al.*, 2022) though these methods are often associated with high production costs (Kakasaheb *et al.*, 2020). The potential of Fe-based catalysts (Fe³⁺/TiO₂), which exhibit catalytic properties similar to platinum in other processes, has not been extensively investigated (Cédric *et al.*, 2021). Furthermore, prior studies have lacked optimization efforts. This research aims to employ solid acid catalysts (Fe³⁺/TiO₂) for the optimization of one-pot transformation of commercial alkaline lignin into aromatic compounds, using central composite design (CCD).

Materials and Methods Materials

Commercial alkaline lignin was purchased from Xian, China. Ethanol (98%) was procured from Hadix, Samaru Zaria, Nigeria. Commercial iron ion/titanium dioxide (Fe³⁺/TiO₂), dichloromethane (analytical grade), and ethyl acetate (analytical grade) were also employed. All other chemicals used in the lignin transformation and analyses were of analytical grade and thus utilized as received without further purification.

Depolymerization of Alkaline Lignin

The conversion experiments were carried out in a 1 L batch reactor. A total of 10 g of alkaline lignin was dissolved in a solvent mixture of water (90 mL) and ethanol (510 mL) with a water-to-ethanol ratio of 3:17 w/w, totaling 600 mL. Diver's quantities of Fe³⁺/TiO₂ catalyst (4.64 g, 6 g, 8 g, 10 g, and 11.36 g) were added to the mixture and charged into the batch reactor. The reactor was operated at temperatures ranging from 200 °C to 213 °C and then cooled to ambient temperature. GC-MS analysis was used to identify the soluble product mixture.

Centrifugation was used for catalyst recovery, and a rotary evaporator was utilized to recover the solvent from the reaction mixture. The commercial alkaline lignin and organic solvent (ethyl acetate (EA)) were employed to separate the organic soluble products (aromatic monomers) from the mixture. The organic soluble product was extracted by dissolving the product mixture in ethyl acetate solvent that the lignin was insoluble leaving behind the lignin. The percentage organic solvent soluble product was calculated by using the solid recovered after evaporating the solvent. (Paresh & Dhepe, 2014).

Design of Experiments

The effects of three variables on the conditions of alkaline lignin depolymerization: temperature (A, °C), titanium dioxide (Fe³⁺/TiO₂) loading (C, g), and operating time (B, minutes) were investigated using a central composite design (CCD). The optimization was done using numerical method. Design-Expert software was used to conduct all statistical analyses.

Characterization

Structural characterization of the commercial alkaline lignin was carried out using Fourier transform infrared spectroscopy (FTIR), specifically with an Agilent Technologies Cary 630 FTIR 8400s equipped with attenuated total reflectance (ATR) for FT-IR analyses in the range of 500 to 4000 cm⁻¹ with a resolution of 4 cm⁻¹. Elemental analysis was performed using Walkley and Black method, flame photometer, atomic absorption spectrometry (calorimeter) and wet digestion method to examine the chemical composition of carbon, sodium, sulphur and nitrogen. Proximate analysis was also performed on the commercial lignin. The XRD analysis of Fe³⁺/TiO₂ catalyst was done with the help of Netherlands, PAN analytical X pert Pro National Steel Raw Materials Explanation Agency (NSRMEA), Kaduna. The diffractor had a duel goniogimeter. The samples scanning were performed from a 2θ value of 5 to 70 ° at the rate of 4.3 °min⁻¹ and the source of X-ray was Cu Ka (1.5418 Å) radiation with Ni filter. Aromatics were identified using an Agilent 7890A GC-MS system (GC: Agilent 7890B; MS: Agilent 5977A).

Results and Discussion.

Commercial alkaline lignin Characterization. Fourier transform infrared spectroscopy (FT-IR)

Functional group analysis of commercial alkaline lignin was conducted using FTIR spectroscopy, as illustrated in Figure 1. A strong, broad band was observed in the range of 3200-3600 cm⁻¹, indicative of O-H stretching frequencies from alcoholic and phenolic hydroxyl groups involved in hydrogen bonding. In the 2850-3000 cm⁻¹ region, strong bands corresponding to the C-H stretching of alkane or alkyl groups were evident. The C-H stretching frequency of alkynes was observed at 2100-2260 cm⁻¹. Bands in the 1700-2000 cm⁻¹ region correspond to aromatic rings, while weak to medium multiple bands between 1400-1600 cm⁻¹ are attributed to C=C groups attached to aromatic rings. Strong bands in the 1000-1300 cm⁻¹ range are assigned to C-O stretching of alkoxy groups, ether linkages, or alcohols. Substitutions on aromatic groups are represented by pattern bands in the range of 670 - 900 cm⁻¹. The band at 1107.0 cm⁻¹ indicated the presence of guaiacyl and syringyl units of lignin. These observations align with trends reported in similar studies, such as those by Raikwar, Majumdar, & Shee, (2019) on commercial alkaline lignin



Elemental analysis of the Commercial Alkaline Lignin

Table 1 presents the elemental composition (carbon, sodium, nitrogen and sulfur) of the commercial alkaline lignin. The commercial alkaline lignin displayed higher sulfur (5.22%), nitrogen (0.65%), and sodium (13.35%) contents. These values align with the findings of Graglia, (2016), who confirmed that pure lignin should have sulfur and sodium contents of less than 5%. The elevated sulfur and sodium levels in the commercial alkaline lignin are due to the kraft method used for its extraction, involving Na₂S and NaOH (Paresh & Dhepe, 2014). The high sodium content in commercial alkaline lignin is associated with a lower hydrocarbon content, resulting in a reduced carbon percentage of 50%, as corroborated by Gordobil *et al.*, (2016), who reported a carbon content of 49.8%.

Table 1. Elemental analysis of commercial arkanne fightin

Properties	Alkaline lignin (%)
Carbon	50.00±0.56
Sodium	13.35±0.05
Nitrogen	0.65 ± 0.01
Sulphur	5.22±0.01

Properties of commercial alkaline lignin

Table 2 presents the density, melting point, ash content, and moisture content of commercial alkaline lignin. The commercial alkaline lignin exhibits a bulk density of 0.5124 g/cm³, a melting point of 200 °C, an ash content of 22.74%, and a moisture content of 3.57%. The higher bulk density, melting point, ash content, and moisture content observed in the commercial alkaline lignin can be attributed to the significant ash content. The elevated melting point of the alkaline lignin is likely due to the presence of sodium and sulphur compounds. The bulk density of the commercial lignin at a bulk density of 0.45-0.60 g/cm³ and melting point of 200 °C. The ash content is in consonance with the investigation of Gordobil *et al.*, (2016) that achieved 22.4%.

Table 2: Physical properties of commercial alkaline lignin

No.	Properties	Alkaline lignin
1	Bulk Density (g/cm ³)	0.5124±0.03
2	Melting point (°C)	200±1.00
3	Ash content (%)	22.74±0.04
4	Moisture content (%)	3.57±0.14

XRD pattern of Iron/Titanium oxide catalyst (commercial). The XRD pattern indicated the presence of titanium oxide and iron oxide, as shown in Figure 2. No sharp diffraction peaks for iron ion were detected in the Fe^{3+}/TiO_2 samples, suggesting that the iron ions are well-dispersed on the titanium oxide carrier. The XRD analysis displayed several sharp peaks, indicative of the catalyst's crystalline nature. These findings are consistent with trends reported in similar studies by Polikarpova, *et al.*, (2022).



Figure 2: XRD pattern of Iron ion/Titanium oxide catalyst (commercial).

Depolymerization of Commercial Alkaline Lignin Response Surface Analysis and Optimization

The experimental design and resulting yields of depolymerization products from the commercial alkaline lignin are detailed in Table 3. The experiments were conducted using a central composite design (CCD) to optimize the parameters for the alkaline lignin depolymerization, with statistical analysis identifying the optimal levels of experimental variables. A quadratic model was selected to accurately represent the experimental data for the one-pot catalytic depolymerization of alkaline lignin into smaller compounds. This model considered the reaction temperature (A, °C), iron ion/ titanium dioxide (Fe³⁺/TiO₂) loading (C, g), and reaction time (B, minutes), as described in equation 1. The coefficient of determination (R² = 0.9197) indicates a strong correlation between the yield of product and the independent variables.

From Table 3, it was observed that increasing the reaction temperature from 200 °C to 210 °C in runs 1 and 2 resulted in an increase in product yield from 15.16% to 18.80% at 60 minutes with a catalyst loading of 6 g, suggesting that higher temperatures enhance the cleavage of thermally unstable ether bonds. This finding aligns with Mankar *et al.*, (2021), who reported increased product yields with rising cleavage of β -O-4 linkages. Similarly, increasing the reaction temperature from 200 °C to 210 °C in runs 3 and 4 led to an increase in product yield from 27.75% to 39.67% at 100 minutes with a catalyst loading of 6 g, indicating that both elevated temperatures and extended reaction times improve ether bond cleavage, consistent with Paresh & Dhepe, (2014).

Experimental runs	Temperature (°C)	Catalyst loading(g)	Time (min)	Response Hydroc. prd (%)
1	200.00	6.00	60.00	15.16
2	210.00	6.00	60.00	18.80
3	200.00	6.00	100.00	27.75
4	210.00	6.00	100.00	39.67
5	200.00	10.00	60.00	21.46
6	210.00	10.00	60.00	21.56
7	200.00	10.00	100.00	16.40
8	210.00	10.00	100.00	17.47
9	196.59	8.00	80.00	8.23
10	213.41	8.00	80.00	21.91
11	205.00	8.00	46.36	5.31
12	205.00	8.00	113.64	25.20
13	205.00	4.64	80.00	48.75
14	205.00	11.36	80.00	25.33
15	205.00	8.00	80.00	24.10
16	205.00	8.00	80.00	24.58
17	205.00	8.00	80.00	23.21
18	205.00	8.00	80.00	24.10
19	205.00	8.00	80.00	22.20
20	205.00	8.00	80.00	22.74

 Table 3: Experimental design and results for the depolymerised commercial alkaline lignin

An increase in catalyst loading to 10 g, however, had a minimal effect on product yield, which increased only slightly from 21.46% to 21.56% at 200 °C, 210 °C and 60 minutes in runs 5 and 6. This suggested that excessive catalyst loading may promote the repolymerization of the depolymerized products, as supported by Mankar *et al.*, (2021). The high density of acidic sites on the catalyst can lead to such repolymerization, reducing the yield of products.

The presence of condensed C–C bond linkages with high bond dissociation energies (384 kJ/mol) acts as a barrier to product yield, as these bonds are difficult to break, corroborating Mankar *et al.*, (2021). Increasing the temperature from 200 °C to 210 °C in runs 7 and 8 with a catalyst loading of 10 g at 100 minutes resulted in a slight increase in product yield from 16.40% to 17.47%, suggesting repolymerization of phenolic dimers at higher catalyst loadings due to increased acidic sites.

In experimental runs 9 and 10, increasing the temperature from 196.59 °C to 213.41 °C at 80 minutes with a catalyst loading of 8 g resulted in an increase in depolymerized products from 8.23% to 21.91%, indicating the critical role of temperature in lignin depolymerization, consistent with Paresh & Dhepe, (2014). Additionally, reducing catalyst loading from 11.36 g to 4.64 g at 205 °C and 80 minutes in runs 14 and 13 increased depolymerized products from 25.33% to 48.75%, implying that lower catalyst dosages reduce condensation reactions and char formation, in agreement with Mankar *et al.*, (2021). Finally, as the reaction time increased from 46.36 to 80 minutes at 205 °C with an 8 g catalyst loading in run 11 and runs 15 through 20, the yield of products increased from 5.31% to 24.10%, 24.58%, 23.21%, 24.10%, 22.20%, and 22.74%, respectively, indicating the significant role of reaction time in lignin depolymerization, as supported by Paresh & Dhepe, (2014). However, further increasing the reaction time to 113.64 minutes at 205 °C with 8 g catalyst loading in run 12 resulted in product yield of 25.20%, with no significant increase, likely due to degradation reactions leading to char formation, consistent with Paresh & Dhepe, (2014).

These trends indicate that product yield was influenced not only by catalyst loading but also by temperature and time variations, aligning with the findings of Paresh & Dhepe, (2014) and Mankar *et al.*, (2021).

Table	4 :	ANOVA	for	the	Response	Surface	Quadratic
Model	dev	eloped for	the	depo	olymerized	alkaline	lignin.

Source		Sum	D	Mean	F	Prob>	
		of	F	squar	Valu	F	
		square		e	e		
		s					
Model		1568.5	9	174.2	12.7	0.0002	Significant
		0		8	3		
	A	103.50	1	103.5	7.56	0.0205	
				0			
	В	244.30	1	244,3	17.8	0.0018	
				0	5		
	С	298.78	1	298.7	21.8	0.0009	
				8	3		
	A^2	155.35	1	155.3	11.3	0.0071	
	- 2			5	5		
	B^2	149.22	1	149.2	10.9	0.0080	
	~	200.00		2	0	0.0010	
	C2	289.80	1	289.8	21.1	0.0010	
				0	8		
	A	6.32	1	6.32	0.46	0.5122	
	В	24.16	1	24.16	2.50	0 1 4 5 2	
	A	34.16	1	34.16	2.50	0.1452	
	C	226.05	1	226.0	16.5	0.0000	
	В	226.95	1	226.9	16.5	0.0022	
Deside	C	126.96	10	5	8		
Residu		136.86	10	13.69			
al Leeleef		105 (7	F	21.12	2.20	0 1022	NT-4
Lack of		105.67	3	21.13	5.39	0.1055	NOT
III		21.10	5	6.24			significant
Pure		31.19	3	0.24			
Cor		1705.2	10				
COI		1705.5	19				
iotai		U					

Table 4 presents the Analysis of Variance (ANOVA) results for the depolymerization of commercial alkaline lignin. The model was statistically significant, as indicated by a p-value (Prob > F) of 0.0002, which was less than the 0.05 threshold. The significant model terms include A, B, C, A², B², C², and BC, while terms AB and AC were not significant. Additionally, the lack of fit was not significant, with a pvalue greater than 0.05. This was further supported by the R² value of 0.9197 shown in Table 5, indicating a high degree of correlation and model reliability.

 Table 5: Significant adequacy test for the model developed for the depolymerized alkaline lignin

Parameters	Values
\mathbb{R}^2	0.9197
Adjusted R ²	0.8475
% error difference	7.9
Adequacy precision	14.054

Additionally, Table 5 showed an adjusted R^2 value of 0.8475 and an adequate precision of 14.054, which exceeded the statistical specification for the signal-to-noise ratio (greater than 4). This indicated the model's robustness and significance. Furthermore, the model's fitness was confirmed by the error difference of 7.9%, as presented in Table 5.

% yield of products for depolymerised commercial alkaline li +24.32 + 2.75 * A + 4.23 * B - 4.68 * C - 3.28 * A² -3.22 * B² + 4.48 * C² + 0.89 * A * B - 2.07 * A * C -5.33 * B * C

Equation 1 presents the products yield model derived from the ANOVA results. This equation incorporates the interactions between temperature (A), operating time (B), and catalyst loading (C). The significance of this model was its capability to predict the product yield under real conditions.





Figure 3A: 3D diagram illustrating the yield of products against time and temperature for the depolymerization of alkaline lignin.

Hdrocarbon



Figure 3B: 3D diagram illustrating the yield of products against catalyst loading and temperature for the depolymerization of alkaline lignin.



Figure 3C: 3D diagram illustrating the yield of products against catalyst loading and time for the depolymerization of alkaline lignin.

Figure 3 presents the response surface and contour plot (3D diagram) illustrating the yield of products as a function of the interactions among independent variables. These visualizations elucidated the influence of reaction conditions on product yield. An increase in reaction time enhances the interaction among lignin structures due to elevated kinetic energy (reactant velocity) at varying temperatures and catalyst loadings (Fe³⁺/TiO₂), thereby increasing its chances of decomposition.



Figure 4: Design-Expert plot comparing the predicted versus actual yields of products for the depolymerized alkaline lignin.

As depicted in Figure 4, the predicted and experimental (actual) data points were predominantly aligned along the regression line, with only a few outliers. This distribution indicated the model's robustness and consistency, corroborated by the R^2 value of 0.9197.

Optimization of the process parameters

As illustrated in Table 6, the process-independent parameters were simulated and optimized to yield two distinct solutions, each characterized by unique process parameter values. The optimization's significance lies in its ability to reduce the number of experimental runs from twenty (20) to two (2), thereby significantly decreasing the experimental workload and operational costs. As detailed in Table 6, Experimental Run 1 specified a catalyst loading of 4.51 g, an operating temperature of 206.23°C, and a reaction time of 86.32 minutes. This configuration predicted an optimized product yield of 51.55%, with a desirability value of 0.931, compared to the desirability value of 0.718 for Optimized Solution 2, which gave product yield of 36.5%. Consequently, Optimized Solution 1 was selected based on these superior performance metrics.

 Table 6: Optimization Solution for the depolymerised alkaline lignin

Ν	Tempe	Cata	Time	Arom	Desira	Valid
0.	rature (°C)	lyst Loa ding (g)	(min utes)	atics (%)	bility	ated (%)
1	206.23	4.51	86.32	51.54 82	0.931	49.54
2	203.24	12.0 0	59.08	36.51 02	0.718	35.61

Identification and Quantification of depolymerized products using GC-MS

The GC-MS analysis of the soluble product from the one-pot catalytic depolymerization of commercial alkaline lignin, as detailed in the total ion chromatogram (TIC) in Figure 5, reveals a variety of compounds. At an optimal temperature of 206.23 °C, the peak area for the produced aromatics reached a maximum of 47.93%. The liquid products were classified into aromatic compounds and aliphatic hydrocarbons based on their composition. The major aromatic compounds identified were N-Vinylpyridinium bromide (5.54%), 4-(Aminomethyl)pyridine (12.11%), 4-Chloropyridine (9.78%), [2,7]Naphthyridine-1,3,6,8-tetraol (9.01%), 1,2-Bis(trimethylsilyl)benzene (4.06%), and 4-tert-Amylphenol (5.17%), in addition to minute quantities of other aromatics were also identified. They were generated through the cleavage of β -O-4 and α -O-4 ether linkages. These findings are consistent with the research by Mankar *et al.*, (2021).

In the aliphatic hydrocarbons, the major detected compounds were 1,3,5-Hexatriene (6.01%), Cyclopropene, 3-methyl-3vinyl- (4.75%), 3-Vinyl-1-cyclobutene (5.36%), Borane diethyl-1-propynyl- (5.67%), Methylphosphorochlorofluoridate (8.24%), Cyclobutane-1,2-bis(methylene)- (9.08%), Butanedinitrile (7.90%), in addition to minute quantities of other hydrocarbon were also identified which were produced via esterification reactions involving ethanol.

These results align with the study by Mankar *et al.*, (2021), which indicated that the presence of aliphatic hydrocarbons suggests that hydrogenation of aromatics via ring-opening reactions may have occurred during the experimental process. Additionally, it was observed that hydrogen for the depolymerization of lignin was derived from ethanol, due to hydrogen's higher bond dissociation energy (104.2 kcal/mol) compared to ethanol's C-H bond dissociation energy (96.1 kcal/mol) (Mankar *et al.*, 2021).





Figure 5: Total Ion Chromatogram (TIC) for optimize depolymerized alkaline lignin at 206.23 $^{\circ}$ C

Conclusion.

The one-pot solid acid catalytic depolymerization of commercial alkaline lignin into aromatic compounds was comprehensively investigated, achieving the major aromatic products such as N-Vinylpyridinium bromide, 4-4-Chloropyridine, (Aminomethyl)pyridine, [2,7]Naphthyridine-1,3,6,8-tetraol, 1.2-Bis(trimethylsilyl)benzene and 4-tert-Amylphenol, revealing significant potential for applications across diverse industries such as pharmaceuticals, polymers, food, herbicides, flavor, detergents, and fragrance. The Fe³⁺/TiO₂ catalyst demonstrated exceptional efficacy, achieving a 47.93% aromatic yield at 206.23 °C, 86.32 minutes, and 4.51 g catalyst loading with the commercial alkaline lignin. The depolymerization process involved the cleavage of B-O-4 and α -O-4 ether linkages. The elemental analysis for the alkaline lignin indicated carbon (50.00%), sodium (13.35%), nitrogen (0.65%) and sulphur (5.22%). The bulk density, ash content, moisture content and melting point of the alkaline lignin were 0.5124 g/cm³, 22.74%, 3.57% and 200 °C. These results demonstrate that the Fe³⁺/TiO₂ catalyst is highly efficient and promising for lignin depolymerization.

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