

Article

Catalytic Co-Pyrolysis of Kraft Lignin with Refuse-Derived Fuels Using Ni-Loaded ZSM-5 Type Catalysts

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Abstract: The catalytic co-pyrolysis (CCP) of Kraft lignin (KL) with refuse-derived fuels (RDF) over HZSM-5, Ni/HZSM-5, and NiDHZSM-5 (Ni/desilicated HZSM-5) was carried out using pyrolyzer-gas chromatography/mass spectrometry (Py-GC/MS) to determine the effects of the nickel loading, desilication of HZSM-5, and co-pyrolysis of KL with RDF. The catalysts were characterized by Brunauer–Emmett–Teller surface area, X-ray diffraction, and NH₃-temperature programmed desorption. The nickel-impregnated catalyst improved the catalytic upgrading efficiency and increased the aromatic hydrocarbon production. Compared to KL, the catalytic pyrolysis of RDF produced larger amounts of aromatic hydrocarbons due to the higher H/C_{eff} ratio. The CCP of KL with RDF enhanced the production of aromatic hydrocarbons by the synergistic effect of hydrogen rich feedstock co-feeding. In particular, Ni/DHZSM-5 showed higher aromatic hydrocarbon formation owing to its higher acidity and mesoporosity.

Keywords: Kraft lignin; refuse-derived fuels; nickel; desilication; catalytic co-pyrolysis

1. Introduction

Renewable energy has attracted increasing attention because of the accelerated fossil fuel exhaustion and growing environmental concerns related to air pollution and global warming [1–3]. Lignin is the main component of lignocellulosic biomass and its amounts have increased due to the development of commercial facilities, such as the pulp industry and bioethanol production process, generating lignin as the process byproduct. Owing to its potential as a fuel or chemical feedstock, many researchers have examined lignin pyrolysis, which is a thermal conversion technology of polymeric materials to gas, oil, and solid residue by heat under a non-oxygen atmosphere [4–6]. Although a large amount of bio-oil can be produced from lignin pyrolysis, most contain monomeric phenols compounds together with oligomeric phenols [7,8].

Owing to the instability of lignin pyrolysis oil, catalytic pyrolysis (CP) has been suggested to produce mono-phenolics or stable aromatic hydrocarbons from lignin [9]. On the other hand, the limited conversion efficiency to the target chemicals and rapid catalyst deactivation is regarded as major problem with its actual commercialization [10]. To overcome this limitation on the CP of lignin, many studies have applied an additional upgrading process to lignin pyrolysis oil, such as hydrodeoxygenation. Lee et al. [11,12] applied the hydrodeoxygenation of bio-oil obtained from lignin pyrolysis to increase the yields of aromatic hydrocarbons and cycloalkanes. The recent trend on the hydrodeoxygenation of pyrolysis oil is to decrease the reaction temperature, pressure, and hydrogen supply required for the sufficient conversion of phenolic pyrolyzates of lignin [13].

One of the other possible ways to produce value-added products from lignin pyrolysis is to increase the production of aromatic hydrocarbons by the addition of hydrogen-sufficient feedstock, such as plastics, to the CP process of lignin. Duan et al. [14] reported that the effective use of hydrogen-sufficient plastics can have a synergistic effect on the aromatic hydrocarbon yield during the CP of lignin. Xue et al. [15] also reported the decreased coke formation using tetralin as the co-feeding material to the CP of lignin.

The value of municipal solid waste (MSW) and waste byproducts of industrial processes, such as lignin, as the feedstock for producing energy has also increased. Refuse-derived fuel (RDF) is a solid fuel made by pelletizing municipal solid wastes consisting of various kinds of wastes, such as paper, plastics, organic wastes, etc. Although RDF can be considered a feedstock of the thermal conversion process for waste treatment and recovering energy, the application for the CP of RDF is limited compared to other feedstock, such as biomass and plastics [16,17].

Whyte et al. [18] reported the CP of RDF using ZSM-5, RDF char, and oyster shell as catalysts. They indicated that ZSM-5 could be applied repeatedly to the CP of RDF by catalyst regeneration and that other catalysts (RDF char and oyster shell) are suitable for the effective deoxygenation reaction. Miskolczi et al. [19] examined the CP of Malaysian RDFs using various catalysts (HY, FCC, ZSM-5, Ni-Mo, Co-Mo catalyst, etc.). They also applied a two-stage CP of RDFs [20]. These studies on the CP of RDF highlight the potential use of RDF as a co-feeding material during the CP of biomass. The higher content of hydrogen in RDF than that in biomass [19,21–23] also suggested that RDF can act as a hydrogen donor to biomass during their catalytic co-pyrolysis (CCP). On the other hand, there has been little systematic research on the CCP of lignin and RDF.

Therefore, the in-situ CP of RDF and the effectiveness of RDF for the co-feeding material during the CP of Kraft lignin (KL) were evaluated using pyrolyzer-gas chromatography/mass spectrometry (Py-GC/MS). Because, recently, Ni catalysts showed good catalytic activity for the production of renewable hydrocarbons [24–26], Ni Ni/HZSM-5 and Ni/desilicated HZSM-5 (Ni/DHZSM-5) were used as the catalysts to determine the effects of Ni and desilication on the catalytic activity of HZSM-5.

2. Results and Discussion

2.1. Properties of KL, RDF, and Catalysts

Table 1 lists the physico-chemical properties, as well as the results of proximate and ultimate analysis results of KL and RDF used as samples in this study. KL had C, O, and H as its main compositional elements. RDF also had a large content of C, O, and H along with small N and Cl contents. Compared to RDF, KL had smaller contents of moisture (M), volatiles (V), and ash (A), whereas its fixed carbon content (FC) was much higher due to its complex network structure and heat resistance [27]. The effective hydrogen to carbon ratio ($H/C_{eff} = (H - 2O - 3N - 2S)/C$) was considered an important parameter for aromatic hydrocarbon production in CP. The H/C_{eff} of RDF was higher than that of KL, as shown in Table 1. This suggests that RDF, a hydrogen sufficient feedstock, could produce larger amounts of aromatic hydrocarbons than KL.

Table 1. Properties of RDF and KL.

	Proximate Analysis (wt. %)				Ultimate Analysis (wt. %)						H/C_{eff}
	M	V	FC	A	C	H	O ^a	N	Cl	S	
RDF	7.2	80.5	2.1	10.2	52.3	7.8	26.9	0.9	1.9	0	0.97
KL	1.5	56.95	39.19	2.36	62.45	5.68	28.25	0.56	0	0.7	0.38

M: Moisture, V: Volatiles, FC: Fixed carbon, A: ash., ^a difference

The Brunauer–Emmett–Teller (BET) surface area and mesopore surface area of DHZSM-5 was larger than those of HZSM-5, indicating the formation of mesopores (average pore size: 8.5 nm,

total pore volume: $0.26 \text{ cm}^3/\text{g}$, mesopore surface area: $140 \text{ m}^2/\text{g}$) due to the desilication of HZSM-5 (Table 2). Figure 1 presents the NH_3 -TPD curves of HZSM-5, Ni/HZSM-5, and Ni/DHZSM-5 showing broad ammonia desorption peaks. For HZSM-5, two main peaks around at 120°C and 360°C can be shown. The lower temperature peak and higher temperature peak represent weak Lewis acid sites and strong Brønsted acidic sites, respectively. Compared to HZSM-5, Ni/HZSM-5 and Ni/DHZSM-5 showed higher acidity at low temperatures because nickel could function as a Lewis acid site. Among the nickel-loaded catalysts, the acidity of Ni/DHZSM-5 was higher than that of Ni/HZSM-5 [28,29]. The increased acidity and mesoporosity of the microporous catalysts by desilication has also been reported [11]. Figure 2 shows XRD patterns of the catalysts, Ni/HZSM-5 and Ni/DHZSM-5. Although Ni/DHZSM-5 showed slightly lower peak intensity than HZSM-5 due to elimination of Si, Ni/DHZSM-5 showed typical MFI-type framework patterns. This confirmed that Ni/DHZSM-5 maintained MFI structure well.

Table 2. Properties of catalysts.

	HZSM-5	DHZSM-5	Ni/HZSM-5	Ni/DHZSM-5
BET surface area (m^2/g)	404	410	368	371

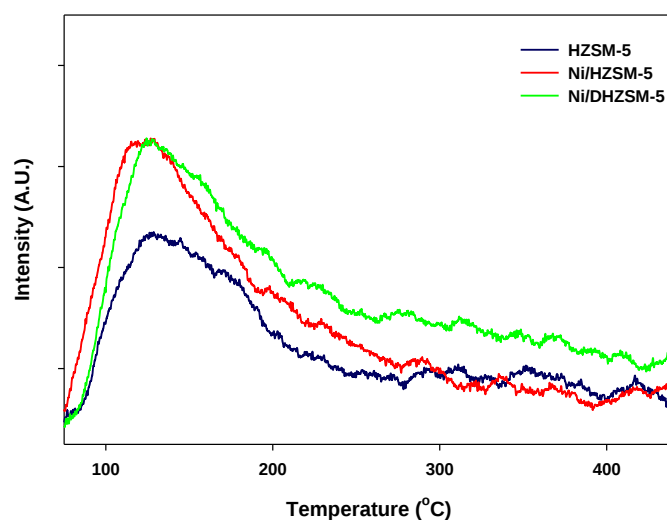


Figure 1. NH_3 -TPD curves of catalysts.

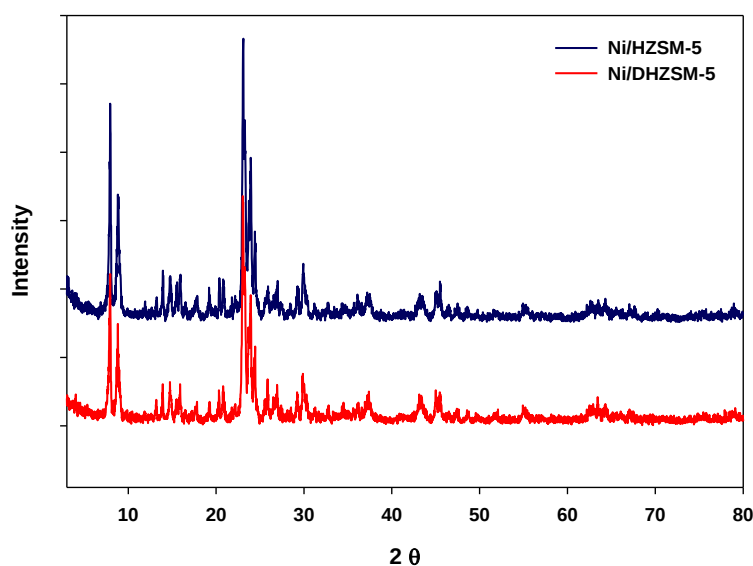


Figure 2. XRD patterns of catalysts.

2.2. Non-CP of KL and RDF

Figure 3 presents the pyrogram for the non-CP of RDF, KL, and RDF+KL. In the pyrolysis of KL, phenolic compounds, such as phenol, alkylphenols, and alkoxyphenols, were produced as the main pyrolyzates. RDF produced the typical pyrolyzates of woody biomass, such as acetic acid, furfural, ketones, levoglucosan, and phenols. Owing to the high contents of fatty acids in RDF, the peaks for alkanolic acids were also monitored on the pyrogram of RDF. These suggested that RDF has a large amount of organic wastes, such as food and fruit peel. The styrene monomer had a higher intensity on the RDF pyrogram, suggesting the presence of polystyrene (PS) polymer in RDF [20]. The co-pyrolysis of KL and RDF pyrogram showed similar pyrolyzates with sum of KL and RDF pyrolyzates without new pyrolyzates.

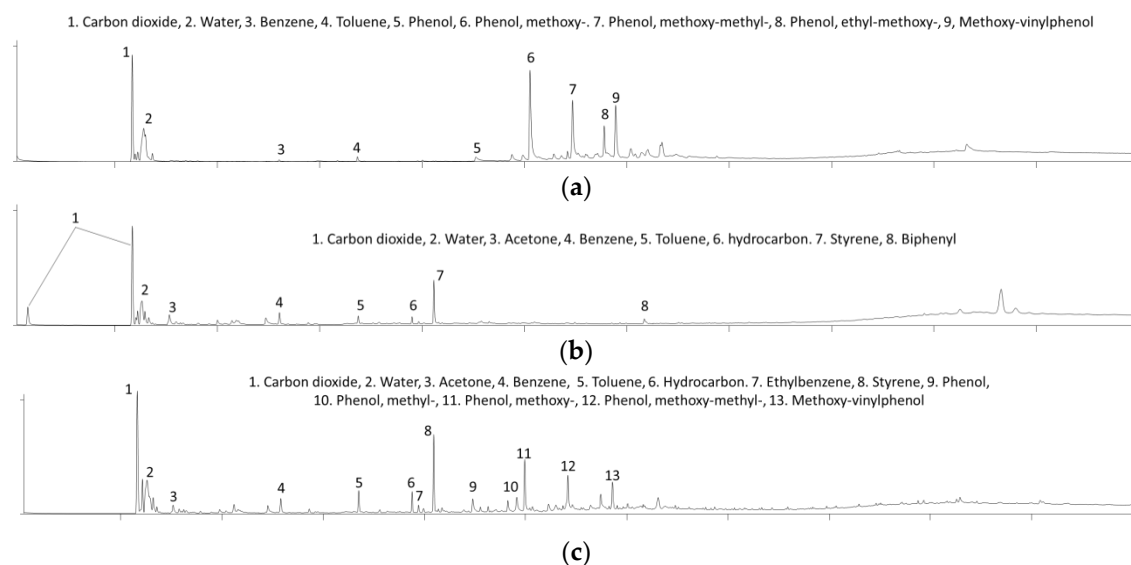


Figure 3. Pyrogram of non CP (a) KL, (b) RDF, (c) RDF+KL.

2.3. CP of KL and RDF

Figure 4 shows the MS peak areas for the main products obtained from the CP of KL over different catalysts used in this study. Compared to non-CP, the CP of KL produced larger amounts of aromatic hydrocarbons, phenol, and alkyl phenols. In addition, the amounts of alkoxy phenols were decreased using the catalysts. Compared to HZSM-5, Ni/HZSM-5 showed higher efficiency on the formation of aromatic hydrocarbons. This indicates that the impregnation of Ni to HZSM-5 can increase the aromatization reaction. Valle et al. [30] reported that the transformation efficiency of oxygenates to hydrocarbons is increased due to the elevated deoxygenation and carbon pool reaction. Iliopoulou et al. [29] also reported that the efficient aromatic hydrocarbon formation can be enhanced by the addition of transition metals, such as nickel and cobalt, because of the increased dehydrogenation reaction on these transition metals. Interestingly, the Ni/DHZSM-5 revealed the highest reaction efficiency on the production of aromatic hydrocarbons and alkyl phenols among the catalysts used in this study. The increased reaction efficiency using the Ni/DHZSM-5 indicates that the reaction efficiency on the CP of KL can be increased not only by the addition of a transition metal, Ni, but also by the desilication of the supporting zeolites. Hong et al. [31] suggested that the mesoporosity of zeolite can be increased by desilication of the microporous catalysts and the desilicated zeolites can provide higher catalytic reaction efficiency because the diffusion efficiency of large molecular reactants is increased due to the presence of mesopores formed by the desilication. The increased acidity of the desilicated catalyst can also increase the overall reaction efficiency of CP. The high reaction efficiency of Ni/DHZSM-5 also suggests that the pore structure and acidity are strongly related to the reaction efficiency.

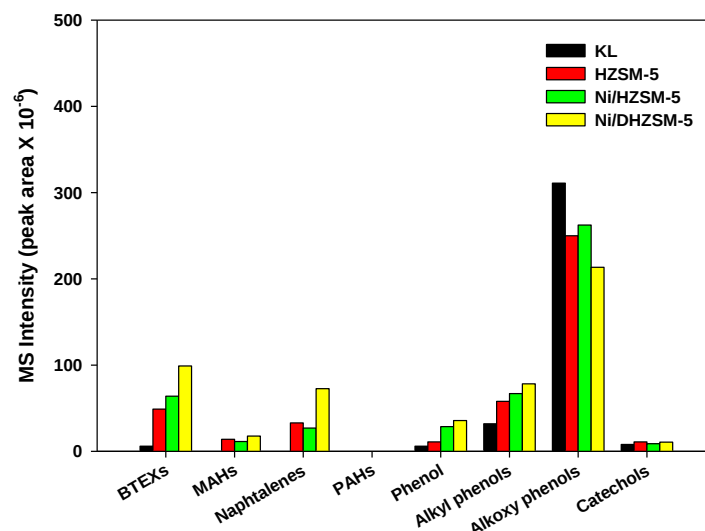


Figure 4. Summed MS peak areas for each chemical groups obtained from the CP of KL over different catalysts. (BTXs: benzene, toluene, ethylbenzene, and xylenes; MAHs; other mono-aromatic hydrocarbons; PAHs; Other poly-aromatic hydrocarbons).

Figure 5 presents the MS peak areas for each chemical group produced from the CP of RDF over different catalysts. Compared to the non-CP of RDF, the CP of RDF over all the catalysts also produced much larger amounts of aromatic hydrocarbons, such as BTXs, styrene, other MAHs, naphthalenes, and PAHs. The CP of biomass and plastics in RDF can be converted to aromatic hydrocarbons via effective cracking, dehydration, decarboxylation, decarboxylation, and oligomerization [32]. The overall efficiency of the catalyst is differentiated by the diffusion efficiency and acidity of the catalysts. Ni impregnation of the zeolite supports can also increase the reaction efficiency of CP of RDF. Although the amount of BTXs obtained from the CP of RDF over Ni/HZSM-5 was larger than that over HZSM-5, the overall summed peak area for aromatic hydrocarbons over Ni/HZSM-5 was smaller than that over HZSM-5, suggesting the decreased reaction efficiency of HZSM-5 after Ni impregnation. The pore blockage of HZSM-5 due to metal impregnation can decrease the reaction efficiency of metal-impregnated HZSM-5 [33]. In addition, the Ni/DHZSM-5 revealed the highest production efficiency of BTXs and naphthalenes than the other catalysts among the catalysts used in this study owing to its pore structure and acidity. This suggests that the combination of the modified mesopore structure of HZSM-5 by its desilication and nickel impregnation can allow better metal dispersion with higher acidity, which can lead to the highest efficiency of aromatic hydrocarbon production during the CP of RDF. This also suggests that DHZSM-5 is a more appropriate supporting catalyst for Ni impregnation without the severe blockage of catalyst pores by Ni particles compared to HZSM-5.

The CP of RDF produced larger amounts of aromatic hydrocarbons than KL over all catalysts. This can be explained by the composition of KL and RDF. KL mainly produces large amounts of phenolic pyrolyzates via a phenolic pool mechanism, leading to large amounts of coke formation. RDF consists mainly of biomass and plastics and can produce large amounts of aromatic hydrocarbons via a hydrocarbon pool mechanism. In addition, RDF has a higher H/C_{eff} ratio than KL, suggesting its hydrogen sufficiency which can be converted more easily to aromatic hydrocarbons than coke.

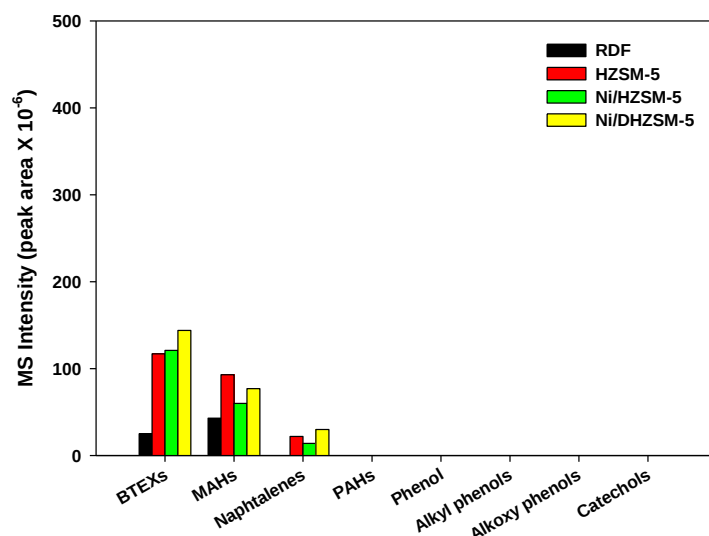


Figure 5. Summed MS peak areas for each chemical groups obtained from the CP of RDF over different catalysts. (BTEXs: benzene, toluene, ethylbenzene, and xylenes; MAHs; other mono-aromatic hydrocarbons; PAHs; Other poly-aromatic hydrocarbons).

2.4. CCP of KL and RDF

Figure 6 shows the MS peak areas for each chemical group obtained from the CCP of KL and RDF over nickel-loaded catalysts used in this study. The amounts of aromatic hydrocarbons and phenolics produced from the non-CCP of KL and RDF (Figure 6) were much larger than those obtained from the individual non-CP of KL (Figure 4) and RDF (Figure 5). This suggests that a more effective cracking reaction of KL and RDF can be achieved by co-feeding KL and RDF at the same time. This can also be explained by the additional depolymerization of lignin due to the additional hydrogen transfer from the components of RDF to KL during their co-pyrolysis. Xue et al. [34] also reported that the addition of PE to the lignin pyrolysis process can promote the depolymerization of lignin and reduce the polymerization and cross-linking of lignin pyrolysis intermediates due to the effective hydrogen transfer in the free radical mechanism.

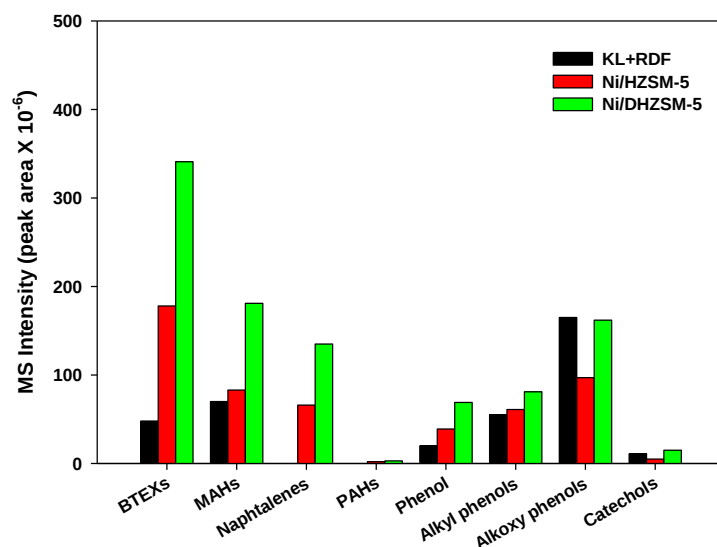


Figure 6. Summed MS peak areas for each chemical groups obtained from the CCP of KL and RDF over different catalysts. (BTEXs: benzene, toluene, ethylbenzene, and xylenes; MAHs; other mono-aromatic hydrocarbons; PAHs; Other poly-aromatic hydrocarbons).

Figure 7 shows the experimental and theoretical MS intensities of the aromatic hydrocarbons and phenolics obtained from the CCP of KL and RDF over nickel-loaded catalysts. As shown in Figure 7, the experimental values of aromatic hydrocarbons, including BTEXs, MAHs, naphthalene, and PAHs were much higher than the theoretical values in both catalysts. This suggests that RDF can be used as an additive feedstock to the CP of KL. The efficient hydrogen donating role of hydrogen-sufficient RDF to hydrogen-deficient KL [35] and the efficient interaction between the CP intermediates of KL and RDF over both catalysts [31] can be explained by the synergistic formation of aromatic hydrocarbons during the CCP of KL and RDF.

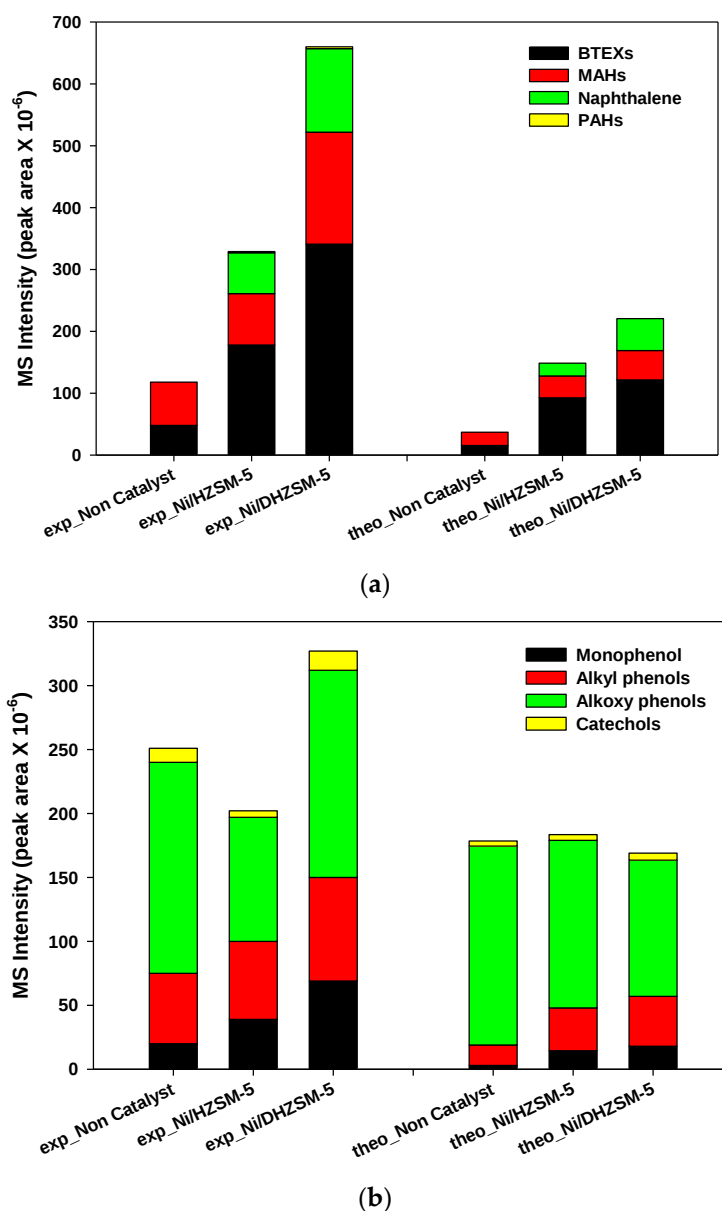


Figure 7. Comparison of experimental and theoretical value of (a) aromatic hydrocarbons and (b) phenolics.

Among two catalysts, Ni/DHZSM-5 showed higher efficiency on aromatic hydrocarbon production during the CCP of KL and RDF than Ni/HZSM-5. This suggests that an effective role of Ni impregnation can be achieved by applying DHZSM-5 as the supporting material because higher acidity can be achieved using mesoporous DHZSM-5.

3. Materials and Methods

3.1. Sample

RDF and KL were obtained from a local company and purchased from Sigma-Aldrich (St. Louis, MO, USA). Both samples were sieved to use the sample with a lower particle size than 300 μm . The sieved samples were dried overnight at 80 $^{\circ}\text{C}$ and kept in a desiccator before all experiments. Proximate and ultimate analysis of KL and RDF were performed to determine their physico-chemical properties according to previously reported method [36].

3.2. Catalysts

Commercial HZSM-5 (CBV 3024, $\text{SiO}_2/\text{Al}_2\text{O}_3$: 30) was used in this study. The desilication of zeolite was performed using the procedure reported elsewhere [11]. The desilication of HZSM-5 was carried out in a 0.2 M NaOH solution. The solution was stirred at 60 $^{\circ}\text{C}$ for 30 min. After ion-exchange using a 0.1 M NH_4NO_3 solution for 12 h with filtration, the catalyst was calcined at 550 $^{\circ}\text{C}$ for 3 h. 5%-nickel-impregnated HZSM-5 and DHZSM-5 were prepared by the wetness impregnation method using nickel nitrate hydrate purchased from Sigma-Aldrich. All prepared catalysts were characterized by N_2 sorption (Micromeritics, Norcross, GA, USA), X-ray diffraction (XRD) (Rigaku D/Max-2000, Rigaku, Tokyo, Japan), and NH_3 -temperature programmed desorption (TPD) measurements (BEL Japan Inc., Toyonaka, Japan). The detailed characterization methods can be found at previous literature [37,38].

3.3. Py-GC/MS Analysis

A conventional Pyrolyzer (Py-2020D, Frontier Lab, Fukushima, Japan) combined with a GC/MS (7890A/5975 inert XL, Agilent Technologies, Santa Clara, CA, USA) was used to perform the thermal and catalytic pyrolysis of KL, RDF and their mixtures. Approximately 1 mg of sample (KL, RDF, or their mixture) was mixed with the same amount of catalyst (approximately 1 mg) in a stainless steel sample cup. The sample was inserted into a preheated pyrolysis furnace at 600 $^{\circ}\text{C}$ and the product vapor was analyzed using the online-coupled GC/MS. The obtained peaks on the pyrogram were identified using a MS library (NIST 8th, National Institute of Standard and Technology, Gaithersburg, MD, USA) search and integrated to compare the amount of each product indirectly [39]. The detailed compounds list showed in Table 3.

Table 3. List of detailed compounds of CP and CCP.

Groups	Compounds	KL	RDF	KL + RDF
BTExs	Benzene	o	o	o
	Toluene	o	o	o
	Ethyl benzene	o	o	o
	Xylene	o	o	o
MAHs	Styrene	o	o	o
	Benzene, trimethyl-	o	o	o
	Benzene, methyl-propyl-		o	
	Indene	o	o	o
	Indene, methyl-	o	o	o
	Indene, dimethyl-		o	

Table 3. Cont.

Groups	Compounds	KL	RDF	KL + RDF
PAHs	Naphthalene	o	o	o
	Naphthalene, methyl-	o	o	o
	Naphthalene, dimethyl-	o	o	o
	Anthracene, methyl-			o
Alkyl phenols	Phenol	o		o
	Phenol, 2-methyl-	o		o
	Phenol, 2,4-dimethyl-	o		o
	Phenol, ethyl-	o		o
	Phenol, methylethyl-	o		o
Alkoxy phenols	Phenol, methoxy-	o		o
	Phenol, methoxy-methyl-	o		o
	Phenol, ethyl-methoxy-	o		o
	Methoxy-vinylphenol	o		o
	Phenol, methoxy-(propenyl)-	o		o
Catechols	Benzenediol	o		o
	Benzenediol, methyl-	o		o

4. Conclusions

The effects of nickel impregnation and desilication on the CP of KL, RDF and CCP of KL with RDF were investigated in terms of aromatic hydrocarbon production. The CP of KL produced large amounts of aromatic hydrocarbons and alkyl phenols with decreasing alkoxy phenols. The CP of RDF having a higher H/C_{eff} ratio than KL produced larger amounts of aromatic hydrocarbons than KL over all catalysts. Compared to Ni/HZSM-5, Ni/DHZSM-5 showed higher yields of aromatic hydrocarbons due to the higher acidity induced by Ni and appropriate mesopore structure by desilication. The CCP of KL with RDF produced larger amounts of aromatic hydrocarbons than the theoretical value in all catalysts via hydrogen donation to hydrogen-deficient KL from hydrogen-sufficient RDF.

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Conflicts of Interest: The authors declare no conflicts of interest.

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