

Co/ACTIVATED CARBON FROM PARASERIANTHES FALCATARIA AS A GREEN CATALYSTS FOR PLASTIC WASTE PYROLISIS

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ABSTRACT

Sengon wood (*Paraserianthes falcata*) is widely used in the sawmill industry. It produces waste that has not received proper handling, furthermore, innovations are needed to solve this problem, as an example as a precursor for catalyst material. This study aimed to synthesize and characterize a Co/activated carbon as a catalyst for LDPE pyrolysis. The method used is the carbonization and activation of sengon wood at 400°C and 800°C using steam, respectively. Carbon was then impregnated with 5% Co(NO₃)₂·6H₂O. Catalyst evaluation was carried out through proximate analysis, benzene adsorption, iodine number, methylene blue adsorption, and catalyst acidity. Functional group content, morphology, crystal phase, and surface area were analyzed using FTIR, SEM-EDX, XRD, and SAA. For application, the ratio of feed: catalyst is 1:1; 1:5; and 1:10. The results showed that the quality of activated carbon was 90% close to Indonesian National Standard quality. The catalyst acidity was 10,555 mmol/g with a metal crystal size of 0.56nm. Surface morphology had opened pores with the pore size, pore volume, and surface area of 2.69 nm, 0.263 cm³/g, and 329.99 m²/g respectively. LDPE cracking using a catalyst resulted in aliphatic, aromatic, and alicyclic hydrocarbon products of 48.86, 15.26, and 12.55%. Co/activated carbon catalyst has an excellent prospect for use as an LDPE cracking catalyst as a green chemical application.

Keywords: Catalyst, LDPE, *Paraserianthes falcata*, py-GC/MS, Steam Activation.

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INTRODUCTION

Sengon wood (*Paraserianthes falcata*) is a renewable natural resource that can be used for various needs, such as building materials, furniture, energy, and activated carbon.^{1,2} Sengon is also widely cultivated by the community, especially in Indonesia, with a total production of 152,014 m³ per year in 2021.³ The benefits of sengon, especially in the sawmill industry, result in sengon wood waste, which needs to be utilized optimally due to environmental pollution.⁴ Sengon wood has an average specific gravity of 0.33 g. It can be used as activated carbon because enriched in cellulose, hemicellulose, lignin, and high oxygen content.⁵

The activated carbon has many applications in various fields, including adsorbents, supercapacitors, soil conditioners, and catalysts.^{6,7,8} Production of activated carbon through chemical activation, such as using HCl, H₂SO₄, ZnCl₂, NaOH, and K₂CO₃, and physical activation using CO₂ or H₂O.^{9,10,11,12} The chemical

activators will produce a better structure with low-temperature treatment, but it has several problems, for not being environmentally friendly and causing secondary pollution. The chemical does not entirely disappear when carbon is washed, then some products cannot be applied in the realm of food and pharmaceutical applications.^{13,14,15} Physical activation with water vapor/steam is considered more energy-efficient, cost-effective, and environmentally friendly because it does not generate chemical waste in the process. However, it can still produce activated carbon with optimal characteristics.

Recently, activated carbon used as matrix support for various purposes to increase the function and effectiveness of activated carbon itself. Several metals are incorporated into the carbon matrix: Fe, Ni, Zn, Cr, and Co. These metals have active sites and are widely used in various applications. The combination of metal and activated carbon has been studied before. Co/activated carbon can be used effectively in the nitrobenzene adsorption process,¹⁶ tetracycline degradation,¹⁷ and peroxy monosulfate activation.¹⁸ Co-/N-doped carbon effectively as catalyst oxidative of desulfurization in fuel upgrading,¹⁹ oxygen reduction activity,²⁰ and hydrolytic dehydrogenation.²¹ Ni-Co sulfide yolk-shell hollow spheres are used for energy storage²² and for hydrogen iodide decomposition catalysts.²³ Supercapacitors are also derived from metal-organic frameworks like metal/activated carbon.^{24,25} The combination of Co/activated carbon has been reported for conversion of feedstock into biofuels and positively affects bio-oils properties.²⁶ The conversion of Macauba pulp oil via deoxygenation reaction-H₂ catalyzed by Co/activated carbon from Macauba endocarp resulting in fractions of gasoline, diesel, and kerosene.²⁷ Co-Phospide/activated carbon from male palm flowers is also converted into bio-jet and green diesel for palm oil conversion.²⁸ CoMo/activated carbon is effective to convert the palm fatty acid distillate (PFAD) into 92% hydrocarbons because of the presence of acid-base sites from metal and activated carbon synergy.²⁹

Another feedstock that can be converted is plastic waste. Plastic known to be converted for various purposes including energy through the pyrolysis process. This method is potential as alternative to solve the problem of plastic waste accumulation and become a new step of renewable energy production. LDPE pyrolysis with a reactor uses high-temperature produce a diesel range of hydrocarbons and low aromatic content.³⁰ The LDPE pyrolysis using a semi-batch reactor produces C₆-C₃₀ with higher proportion of alkanes and alkenes but it has a lower content of acids, alcohols, benzene, and ketones.³¹ The fixed bed reactor used for LDPE pyrolysis with a carbon-based catalyst to produce the hydrocarbon jet fuel fraction.³² Sriningsih *et al.*,³³ using a Co-Mo/Z catalyst in cracking LDPE plastic, produce 71.49% gasoline and 28.52% diesel fuel. The methods and tools in previous studies require a difficult and long operating time, therefore, it is necessary to modification of pyrolysis modeling using fast, short, and more practical instruments to determine the process and results of LDPE pyrolysis as a first step in estimating the product. One of the pyrolysis methods is using Py-GC/MS, which has a short operation time and a more comprehensive range. It has been used as an instrument to increase the quality of algae pyrolyzed using HZSM5-SiO₂/Al₂O₃ catalysts.³⁴ The py-GCMS method is also used for the catalytic reaction between spirulina and zeolite feeds to produce C₁₇-C₂₀ hydrocarbons which are commonly used as fuel.³⁵ Pyrolytic research using a py-GCMS instrument with LDPE as a feedstock and steam-activated metal-carbon catalyst (Co/activated carbon) from sengon wood waste has never been carried out. Based on this description, a study was conducted on fast catalytic pyrolysis with LDPE as feedstock and Co-activated carbon assisted from sengon wood waste as a green catalyst for LDPE conversion.

EXPERIMENTAL

Materials

Raw material used in this study were sengon wood waste from Bogor-Indonesia, Co(NO₃)₂.6H₂O (Merck-Darmstadt, Germany), Low-Density Polyethylene (LDPE) plastic, distilled water, 0.1 N sodium thiosulfate (Merck-Darmstadt, Germany), 0.1% iodine solution (Merck-Darmstadt, Germany), methylene blue (Merck Darmstadt Germany), benzene (Smart lab, Ltd. Comp- Tangerang, Indonesia), and starch.

The equipment used was Iwaki's beaker, 100 mL Iwaki Erlenmeyer, 50 mL Pyrex burette, 25 mL and 10 mL volume pipette, glass plate, spatula, Memmert oven, Ney Vulcan furnace D-550, Ohaus analytical balance, stirrer, DLab hot plate MS-H280-Pro, and aluminum foil. The instrument for characterization analysis was Fourier Transform Infrared (FTIR) using Thermo Scientific Nicolet iS5 ATR iD7 Diamond, py-GC-MS Shimadzu QP2010, UV-Vis spectrophotometer with Shimadzu UV-1700, X-Ray Diffraction

(XRD) X'pert PRO PANalytical, Scanning Electron Microscope-Energy Dispersive X-Ray (SEM EDX) Bruker XFlash Detector 4010, and Surface Area Analyzer (SAA) Meso 112-JWGB.

Research Procedure

The method of this study consisting of several stages, namely carbonization-activated carbon production from sengon wood waste, wet impregnation using $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, and application of the catalyst product to LDPE plastic using GC-MS pyrolysis.

Activated Carbon Production

The first step is the preparation of sengon wood waste. Sengon wood is cleaned from impurities that may be attached to the wood until it is clean. Then it is cut 5 cm x 5 cm and dried at a temperature of 110°C for 24 hours. Sengon was carbonized at 400°C for 5 hours resulting in carbon product. The carbon then crushed to form a powder. After being in the powder form, it is then filtered with a 60mesh sieve. The carbon that has been sieved is then activated using steam (water vapor) at 800°C for 90 minutes. The activated charcoal obtained is then stored in a desiccator to keep it dry.

Impregnation of Activated Carbon with $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$

$\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ has been diluted with distilled water added with activated carbon in a 250 mL Erlenmeyer flask. The mixture was refluxed at 80°C using a hot plate magnetic for 2 hours and stirred at 200 rpm. After that, it was filtered through a Buchner filter size 41, dried and calcined at 500°C for one hour. The Co/activated carbon catalyst stored in a desiccator.

Catalytic Pyrolysis of LDPE using py-GCMS

LDPE plastic was prepared by washing, drying, and cutting into pieces. The 0.4 mg LDPE put into a capillary tube and added 0 mg, 0.4 mg, 2 mg, and 4 mg of Co/activated carbon catalyst (ratio of 1:0, 1:1, 1:5, and 1:10). The pyrolysis tube was inserted into the Py-GCMS instrument and pyrolyzed with a flow rate of 46.5 mL/min, using linear velocity and purge flow of 23.7 cm/sec and 3.0 mL/min at 500°C, respectively. Helium flow rate and temperature oven set up for 3 mL/min and 50°C, respectively.

Proximate Analysis

evaluation products were conducted following the Indonesian National Standard (SNI) of carbon (SNI 1683-2021) and activated carbon (SNI 06-3730-1995).

Moisture Analysis

Two g of sample is put in an evaporating cup, each of which has been prepared in the oven for 1 hour, then the sample is heated at 110°C for 4 hours.

$$\text{Moisture (\%)} = \frac{M_2 - M_3}{M_2 - M_1} \times 100\%$$

Volatile matter analysis: the sample is weighed again, then covered with a lid, put into the furnace, and then heated at 900°C for 10 minutes.

$$\text{Volatile matter (\%)} = \frac{M_2 - M_3}{M_2 - M_1} \times 100\%$$

Ash content analysis: the sample is weighed again as in the previous step and placed in the furnace at 750°C for 6 hours.

$$\text{Ash content (\%)} = \frac{M_3 - M_1}{M_2 - M_1} \times 100\%$$

$$\text{Fixed carbon (\%)} = 100\% - \text{ash and volatile matter content}$$

Benzene Analysis

The sample is weighed as much as 2 g with a petri dish, then put into the desiccator where 100 mL of benzene is placed underneath; close the desiccator and let stand for 24 hours.

$$\text{Benzene (\%)} = \frac{M_3 - M_2}{M_2 - M_1} \times 100\%$$

Where, M_1 = crucible weight (g)
 M_2 = crucible+sample before treated(g)
 M_3 =crucible+sample after treated (g)

Iodine Number Analysis

A total of 0.25 g of sample was weighed and heated in the oven for 1 hour, then 25 mL of iodine was added, stirred for 15 minutes, and filtered. Pipette 10 mL of sample, give three drops of starch indicator and titrate the solution using 0.1N sodium thiosulfate until the solution turns colorless.

$$\text{Iodine number} = \frac{V1 - ((V2 \times N \text{ Na}_2\text{S}_2\text{O}_3) : N \text{ iod} \times M \text{ 12})}{M} \times \text{FP}$$

Where, V1 : I₂ volume
 V2 : Na₂S₂O₃ volume
 N: normality
 M: mass of activated carbon

Methylene Blue Analysis

The sample is weighed as much as 0.25 g and heated in an oven for 1 hour. The sample added with 100 ppm methylene blue, stirred for 30 minutes, and filtered. One mL of sample diluted with distilled water and analyzed with a UV-Vis.

$$\text{Methylene blue adsorption (mg/g)}: \frac{1200 - (cxFP) \times v}{M}$$

Where, c: concentration
 FP: dilution factor
 V: volume

Characterization of Co/Activated Carbon from Sengon Wood Waste

Several analyzes using instruments were conducted, including FTIR, SEM-EDS, XRD, and SAA to determine functional groups, morphology, phase, surface area of catalyst, respectively.

RESULTS AND DISCUSSION

Co/activated Carbon Catalyst Properties Using Steam Activation

Activated carbon production started with a pyrolysis process or carbonization at 400°C for 5 hours under limited oxygen conditions. The carbonization process in carbon formation uses incomplete combustion to produce carbon products and liquid smoke due to pyrolytic vapor condensation. After carbonization, the carbon was activated using steam/water vapor to increase the quality of carbon (opening carbon pores and increasing the surface area). The results of carbonization and activation of sengon wood waste produce 56.63% yield of raw materials and 65% of carbon. In order to get the combination of activated carbon and Co metal, the wet impregnation method was used to insert this metal into carbon pores. The product characterization of carbon, activated carbon, and catalyst Co/activated carbon are shown in tables and figures, which will be explained later. Mass shrinkage is influenced by various factors, including raw materials, reaction temperature, and reaction time. The quality analysis of carbon and activated carbon compared with SNI, as shown in Table-1.

Table-1: Carbon and Activated Carbon Proximate from Sengon Wood Waste Compared to the SNI Carbon and Activated Carbon

No	Testing parameters		Sengon wood carbon	SNI wood carbon No. 1683-2021	Sengon wood-activated carbon	SNI activated carbon No.06-3730-1995
1.	Moisture (%)		5.77	8-10	12.18	<15
2.	Volatile matter (%)		27.55	10-17	8.30	<25
3.	Ash (%)		3.54	<4	18.62	<10
4.	Fixed carbon (%)		68.91	>79	73.07	>80
5.	Benzene (%)		13.32	>25	7.15	>25
6.	Iodine number (mg/g)		109.84	>200	644.95	>750
7.	Methylene blue adsorption (ml/g)		28.098	>60	30.86	>60

From the Table-1, the activated carbon quality is 90% close to the quality required by SNI. From the data, the moisture of activated carbon is higher than carbonization products, perhaps because activated carbon

has a finer texture with more open pores making it easier to absorb water from the air, thereby increasing the calculated water content.³⁶ Carbonization treatment at high temperatures will increase the carbon content but reduce the volatile matter. These results follow Aworn's,³⁷ where the trend of increasing carbon content and decreasing volatile matter occurs with the carbonization treatment of various biomass raw materials. This condition is ensued of the carbonization treatment with a dehydration process or water removal process. There is a process of decomposing lignocellulose into carbon elements and releasing non-carbon compounds in that process.

The quality of carbon increased significantly after the steam activation process, as seen from the increase in carbon content, decrease in ash content, and especially the five times increase in the iodine number. Likewise, the adsorption capacity of methylene blue increased after the activation treatment. This result occurs due to the reaction of water vapor/steam with carbon leading to the opening of carbon pores and expanding the surface area, which will increase the ability of activated carbon to adsorb iodine compounds and methylene blue. The adsorption capacity of iodine and methylene blue are widely used as indicators in determining activated carbon quality. These test parameters are also derived from ASTM D4607-14 and ASTM C837-99. The iodine number parameter may be used to estimate the surface area of several types of activated carbon. In contrast, methylene blue can be used as an indication of the adsorption capacity of activated carbon for molecules with similar dimensions to methylene blue, as well as predicting the active site of the material.³⁸ An analysis was carried out using FTIR based on the frequency of absorption bonds, and the intensity of the transmittance is related to the presence of an element. This instrument is used to find out the functional groups of the product. The functional groups of the sample were recorded between 4000-400 cm^{-1} using the FTIR Thermo Scientific Nicolet iS5 with the ATR technique. Data from FTIR analysis results from carbon, activated carbon, and Co/activated carbon samples are presented in Fig.-1.

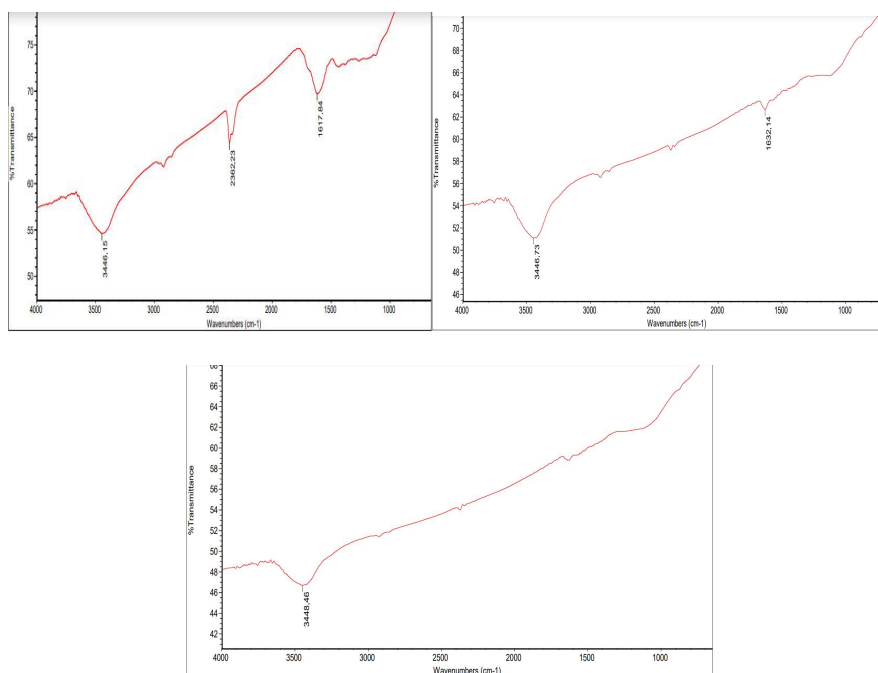


Fig.-1: FTIR Spectra of Carbon, Activated Carbon, and Co/activated Carbon

From the Fig.-1, there was alteration in the spectra of the three samples. The processes of carbonization, activation, and impregnation treatment lead to simpler dehydration and decomposition of the sample functional groups.³⁹ OH functional group showed at 3446-3448 cm^{-1} .^{40,41} While the C=C aromatic bonds that make up hexagonal carbon and activated carbon at wave number 1617-1632 cm^{-1} . The triple carbon bonds are found at a wave number 2362 cm^{-1} due to carbonization and activation processes.⁴² These results also follow the reference to how to interpret FTIR in a compound.⁴³ Using the XRD instrument for the phase analysis on carbon, activated carbon, and Co/activated carbon catalysts described below (Fig.-2).

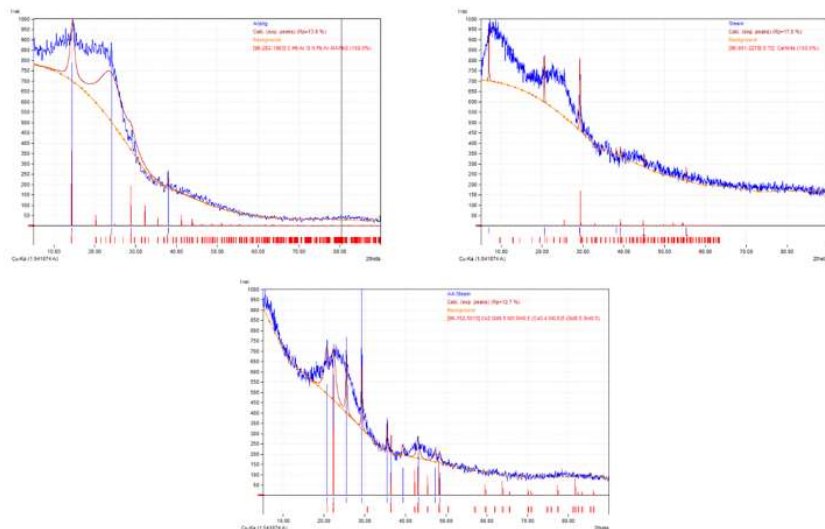


Fig.-2: The XRD Analysis of Carbon, Activated Carbon, and Co/Activated Carbon from Sengon Wood Waste Using Steam Activation

Table-2: Interlayer Spacing of the Samples

Sample	Pos. [$^{\circ}$ 2Th.]	FWHM Left [$^{\circ}$ 2Th.]	d-spacing [$\text{\AA}$]	Rel. Int. [%]
Carbon	14.6689	0.8029	6.03896	72.57
	24.1588	0.4015	3.68399	100.00
	37.9745	0.2007	2.36951	74.26
Activated carbon Co/activated carbon	29.3000	0.2007	3.04822	100.00
	36.4913	0.2676	2.46234	100.00
		0.4015	4.27325	6.64
		0.4015	3.47598	6.64
		0.2007	3.04511	22.78
	20.7873	0.2007	2.52227	22.78
		0.1004	2.45892	21.35
	25.6284	0.4015	2.28515	21.35
		0.2007	2.09945	100.00
	29.3306	0.4015	1.91954	100.00
		0.3346	1.87963	51.75
	35.5947			51.75
	36.5438			31.82
	39.4332			13.69
	43.0871			16.05
	47.3596			12.77
	48.4290			13.64

Figure-2 and Table-2 show that the carbonized and activated sengon wood sample has a broad peak shape at 2θ around 23 and 43° , which describes an amorphous carbon type with little crystal structure and refers to the crystal plane of the graphite layer. This result follows the carbonization result from other findings.⁴⁴ The metal impregnation process on activated carbon shows that the structure has not changed significantly and still has amorphous, random, and irregular shapes. Co-metal is usually seen at peaks of 44.2° and 51.5° with a concentrated cubic structure phase, while a peak of 37° indicates the presence of Co_3O_4 .²⁷ However, in this study, these peaks did not appear precisely because the metal had been dispersed evenly into the

activated carbon pores, or it could be due to the amount of metal that entered being so small that the instrument did not detect it. In order to evaluate the morphology and metal content confirmation, we use SEM-EDX as an instrument. Analysis of surface morphology and content of the samples was then examined by the SEM-EDX instrument (Fig.-3).

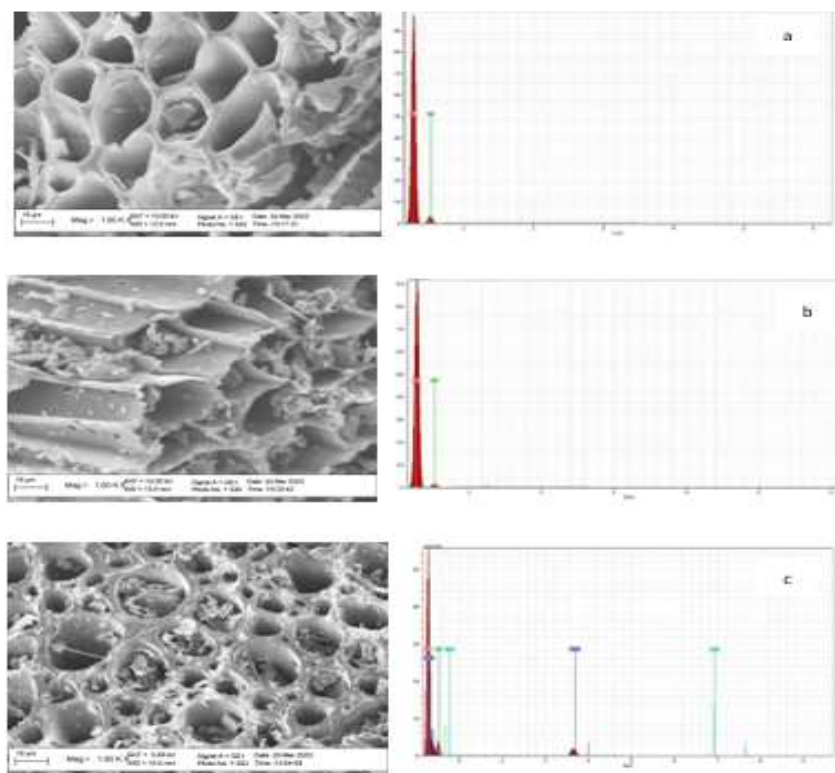


Fig.-3: SEM EDX Analysis of Carbon, Activated Carbon, and Co/Activated Carbon from Sengon Wood Waste with Steam Activation

SEM used to evaluate the sample morphology of raw material to activated carbon as a result of treatment. SEM micrograph runs with 1000x magnification (Fig.-3). All the samples displayed, whether carbon, activated carbon, or Co/activated carbon, showed pores on their surface. There is a difference in the size of the pores and the lane, like a honeycomb overlapping one another. It is accordance with the activated carbon from Merbau wood waste synthesized by Santi *et al.*⁴⁴ The analysis results indicate a peak indicating the Co metal content after the metal impregnation treatment. From this result, the metal Co has been successfully impregnated on activated carbon. BET and BJH methods was used for surface area, pore volume, and average pore size analysis. The analysis was carried out by degassing process, so the sample is ready to adsorb N₂ gas. The adsorption and desorption isotherm curves of N₂ in each sample and a graph of the sample pore distribution are presented in Fig.-4.

From Fig.-4, the adsorption and desorption isotherm curves of N₂ in carbon, activated carbon, and Co/activated carbon samples follow isotherm III, a combination I and IV, and type I, respectively. Changes in isotherm type occur as the sample is treated. After the steam activation process, the activated carbon shows a type I and IV isotherm pattern with a sharp increase in P/P₀ below 0.1 and a hysteresis loop at pressure P/P₀=0.5. This pattern occurs due to the condensation and evaporation of mesoporous capillaries, so it can be estimated that activated carbon tends to contain microporous-mesopores types. After the metal impregnation process, the isotherm pattern changed so that it characterizes the majority of the new micropores formation, due to the metal impregnation process. Co/activated carbon catalyst has a smaller pore size than carbon and activated carbon (Table-3). The Co metal impregnation process partially closes the mesopore pores and forms new pores, followed by an increase in surface area.

This can be seen from the small size of the metal so that it can enter the meso-sized pores. Overall, from the data, the average pore diameter of the sample is 2-19 nm and it can be classified into the microporous-

mesopore class according to IUPAC provisions (micropores: <2 nm; mesoporous: 2-50 nm; macropores >50 nm). This is also supported by the BJH pore distribution curve, where most pores are distributed over 2 nm in size.

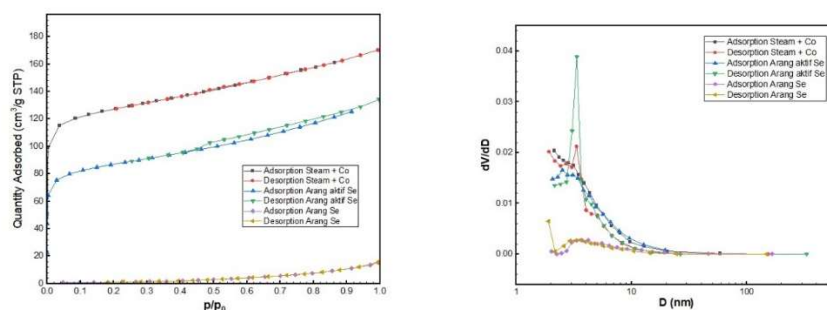


Fig.-4: Adsorption-Desorption Isotherm of N₂ analysis (a) and BJH Pore Distribution of Carbon, Activated Carbon, And Co/Activated Carbon from Sengon Wood Waste with Steam Activation

Table-3: The Surface Area, Acidity, and Average Metal Size of the Catalyst

Sample	S _{BET} (m ² /g)	V _{tot} (cm ³ /g)	D _{average} (nm)	Acidity (mmol/g)	Metal average size (nm)
Carbon	4.797	0.024	19.686	6.065	
Activated carbon	278.223	0.206	2.964	8.439	
Co/Activated carbon	392.999	0.263	2.679	10.555	0.56

From the Table-3, the carbon surface area increased after activation and impregnation treatment. It occurs due to the heating process and activator role. In the carbonization process, there are still impurities, minerals, tar, and oxides that have not been released from the carbon. In contrast, the activation process can further open the pores and increase the surface area because it can bind these compounds out of them.⁴⁵ With the activation and impregnation processes, the carbon surface area increases significantly, followed by forming a new pores, which lead the acidity increases. The metal Co-impregnation process affect the increasing of catalyst acidity. This occur because the empty orbitals on the metal will accept the electrons (serve as Lewis's acid sites) from ammonia. High acidity is influencing the catalytic pyrolysis.

Catalytic Pyrolysis of LDPE Using Co/Activated Carbon from Sengon Wood Waste

Pyrolysis is a process of organic material degradation using several inert gases such as helium, argon, and nitrogen. The pyrolysis process conducted with or without a catalyst, generally at 350-900°C, and produces fuels such as gasoline and diesel.³⁰ Chemical identification in product were carried out using py-GCMS. From the data, it is possible to check and classify chemical compounds and their relative concentrations semi-quantitatively so the activity and selectivity of the Co/activated carbon catalyst in the LDPE pyrolysis can be predicted. The ratio of feed/catalyst is 1:1; 1:5; and 1:10, where pyrolysis is carried out without a catalyst and it becomes the basis/control for the effect of using a catalyst in reaction process. As many as 25-45 chemical compounds can be identified from the reaction process product. From all of them, we separate these compounds into several groups, namely alcohols, aldehydes, ethers, carboxylic acids, polycyclic aromatic hydrocarbons, aromatic hydrocarbons, alicyclic hydrocarbons, and aliphatic hydrocarbons. Alcohol, aldehyde, and ester products are the hydrocarbon oxidation products.³⁰ The pyrolysis results showed of peaks corresponding to the various characteristics of certain chemical compounds, where compounds with low molecular weights would appear at a shorter retention time then compounds with high molecular weights. Data on the composition of chemical compounds formed from catalytic pyrolysis results are presented in Table-4.

From the Table-4, several compounds were found in the LDPE catalytic pyrolysis products. In general, plastics are long-chain polymers and have a low density. As the name suggests, LDPE is composed of polyethylene compounds from petroleum and is known as a thermoplastic. The distribution of pyrolysis

products depends on various factors, including feedstock, temperature, time, and heating rate. This result is evident from previous studies that mixed LDPE with biomass-produced products with different compounds, especially in producing aromatic compounds.⁴⁶

Table-4: The Chemical Compound of LDPE Pyrolysis

Chemical compound	Name	Retention time (min)	Conc. Relative (%)			
			LDPE	1:1	1:5	1:10
Alcohol	1-hentetracontanol	23.95	17.30	7.05	-	-
	1.30-Triacontanediol	26.75	-	0.52	-	-
	2-Butyl-1-octanol	15.18	15.92	16.49	-	-
	9H-Fluorene-9-methanol	20.54	-	-	-	2.62
	Dihydrophytol	35.15	-	0.33	-	-
	Heptacosanol	20.94	31.3	-	-	-
	n-Eicosanol	31.55	-	1.08	-	-
	n-Hentriacontanol	40.51	-	0.55	-	-
	n-Pentacontanol-1	29.14	13.26	-	-	-
	n-Hentetracontanol-1	27.65	-	-	-	-
	Stenol	29.65	-	0.57	-	-
Aldehyde	2-Chlorohexanal	9.87	-	-	-	2.53
Aromatic hydrocarbon	1.3.5-Trimethylbenzene	14.96	-	-	-	0.14
	1-Metil-2-N-hexylbenzene	21.86	-	-	-	0.86
	11-Benzylheneicosane	41.79	-	0.34	-	-
	Benzene	17.68	-	-	1.17	1.03
	Benzene. dodecyl-	25.89	-	0.38	0.33	-
	Benzene. eicosyl-	28.45	-	0.18	1.00	-
	Benzen.hexadecyl-	24.90	-	-	0.58	-
	Hexane. 2-phenyl-3-propyl	20.44	-	-	2.76	-
	Mesitylethylene	16.67	-	-	0.75	0.82
	o-Ethyltoluene	14.31	-	-	-	3.45
	o-Xylene	13.91	-	-	2.86	4.36
	Toluene	11.31	-	-	4.00	5.52
	3.3-Dimethylindene	17.66	-	-	1.31	-
	9-Methylfluorene	21.54	-	-	-	2.24
	Oxirane. 2-2-diphenyl	22.06	-	-	0.50	-
Ether	Cinnamyl propyl ether	21.82	-	-	1.18	-
Alicyclic hydrocarbon	Cyclopropane	6.48	9.90	5.39	12.55	-
	cycloheptadine	-	-	-	-	2.01
Long-chain hydrocarbon	n-Heptaconsane	30.95	-	-	-	0.28
	n-Hexatriacontane	19.56	-	3.58	-	0.79
	n-Pentatriacontane	20.27	-	14.55	16.36	8.42
	n-Tetratetracontane	20.95	-	38.67	3.91	3.91
	Tetrapentacontan. 1-54-dibromo	48.84	4.03	3.42	2.29	-
	Octatriacontane. 1.38-dibromo	35.91	-	2.87	-	-
	Tetratriacontane	22.29	-	-	-	2.90
PAH _s	1.3-dimethyl naphthalene	19.31	-	-	1.59	-
	1.7-dimethyl naphthalene	19.31	-	-	-	1.37
Carboxylic acid	Oleic acid	22.45	1.25	-	-	-
	Oxalic acid	6.47	9.90	-	-	13.02
Aliphatic hydrocarbon	1-Chlorodecane	12.76	-	-	3.14	-
	1-Chlorododecane	14.11	-	-	-	10.59
	1-Chlorooctane	12.80	-	-	-	4.15
	1-Chlorohexadecane	17.99	2.85	-	-	11.14
	1-Decene	13.98	2.34	-	-	-
	1-eicosene	28.09	-	0.36	-	-

10-Metileicosane	19.56	-	-	-	1.90
2-Metilpentane	7.48	-	-	0.36	-
2-phenyl-2.3-hexadiene	18.39	-	-	0.57	0.43
3-Methylheneicosane	25.12	-	0.32	-	-
9-Tricosene	25.65	-	0.59	-	-
Adacene 12	12.60	1.52	2.76	-	-
Cetene	18.39	0.33	-	-	-
n-Dodecane	16.24	-	-	5.52	-
n-Eicosane	18.02	-	-	4.86	5.07
n-Heptadecane	20.28	-	-	-	1.77
n-Hexadecane	19.56	-	-	4.37	-
n-Pentadecane	18.81	-	-	5.41	5.74
n-Tetradecane	20.96	-	-	2.31	1.98
n-Tricosane	20.27	-	-	5.22	-
n-Tridecane	17.16	-	-	1.98	-
Nonadecane	24.25	-	-	1.60	-
Octadecane	20.96	-	-	0.80	-
Silane	7.06			10.72	
Tetradecane. -1chlorol	14.08				

LDPE has a volatile substance content of 100% with a higher percentage of hydrogen than sugarcane bagasse. It also has quite a lot of hydrogen, 14.28%.³¹ As in principle, the pyrolysis process will crack the complex compounds into simpler/smaller, intermediate, and final product compounds. Hydrocarbon compounds are more desirable for alternative energy as products of pyrolysis results, while compounds containing oxygen, nitrogen, and PAHs tend to be undesirable. The reason is that hydrocarbon compounds can be a source of energy, so the fuel must contain high octane or cetane number. Vice versa, the presence of oxygenated compounds will reduce the quality of the product because it will interfere with the combustion process. Acidic compounds are also not preferred in biofuel products because they cause corrosion and are non-effective in energy consumption. The LDPE feedstocks can produce aliphatic hydrocarbons and result in the formation of saturated (long-chain) hydrocarbons. This is per the results of Dewangan's study,³¹ where the use of LDPE increased the aliphatic content (26.08%), reduced phenol to 24.96%, alcohol to 14.55, and acid to 8.96%. LDPE can improve bio-oil quality because deoxygenation and denitrogenation reactions occurred.⁴⁷

From Fig.-5, in pyrolysis without a catalyst, most produce alcohol compounds, while the hydrocarbon products are minimal compared to using a catalyst. In using a 1:1 catalyst, long carbon chain products are the majority, then alcohol compounds are formed, but not as much as in pyrolysis without a catalyst. Aromatic, aliphatic, and alicyclic products began to form, although not optimally, each around 0.9, 4.63, and 5.39%, respectively. The catalyst has notable role in the reaction process, which can facilitate the breakdown or LDPE cracking into hydrocarbon products. On the other hand, catalyst with a ratio of 1:5 and 1:10 gave a prominent increase in the production of hydrocarbons. At a ratio of 1:5, aromatic, aliphatic, and alicyclic hydrocarbons of 15.26, 48.8, and 12.55%, respectively, while using a 1:10 catalyst produces these products of 18.42, 42.77, and 2.01%. Fuel compounds such as gasoline, diesel, and kerosene are generally in the group of aliphatic hydrocarbon compounds. The catalyst has a positive influence on the distribution and selectivity of the desired product. The increase in catalyst weight also affects the quantity and quality of the product. The greater of the catalyst used, could increase the active site number, facilitate intermediate product and the active site contact, therefore the catalyst activity and selectivity increase to an optimum level. These results are consistent with previous studies that carried out spirulina py-GCMS using zeolite, where a catalyst significantly affected 13 times more hydrocarbon products than without a catalyst.³⁵ The catalyst has an active site and large pores provided by the metal and the surface area of activated carbon therefore the reaction process between the reactants and the pyrolysis occurred. However, too large pores sometimes make it difficult for mass transfer between the intermediate product of pyrolysis and the catalyst to form high coke. From the data on the characteristics of the catalyst, it was found that the acidity, pores, and surface area of the Co/activated carbon catalyst were higher than the carbon and activated carbon itself.

The synergy of pores and active sites on the catalyst is also considered to facilitate aromatization reactions, in which aliphatic compounds are converted into aromatic compounds. According to Duang,³² the reaction mechanism in converting polymers such as LDPE into simple hydrocarbons is dehydrogenation, aromatization, and hydrogen transfer reactions, which are assisted by the active site of a catalyst. Depolymerization of long-chain aliphatic to light alkene compounds is also a route for aromatic compounds forming. Due to a higher density value, pyrolysis products generally have a lower cetane number than commercial products, making them more suitable for fuel for power generation and heating. According to US EPA standards, the total aromatic content in fuel, especially diesel fuel, should not exceed 20%. The more aromatic content in the fuel will lead to lower cetane or octane number. The low content of hydrocarbons in pyrolysis products without a catalyst proves that the catalyst is a strategy to improve product quality by reducing oxygen, nitrogen, and carcinogenic compounds. That way, the yield and selectivity of pyrolysis products increased and the catalyst is considered applicative. Metal-impregnated activated carbon has acid sites, surface area, and pores, so it can be a facilitator for producing hydrocarbon products and reducing oxygenated fuel products. Pyrolysis is allegedly an environmentally friendly method. However, it still leaves constraints on product quality, such as high oxygen content causing stability and corrosion problems, low combustion rate, and calorific value, so strategic steps for future research are needed to improve the quality of pyrolysis products.

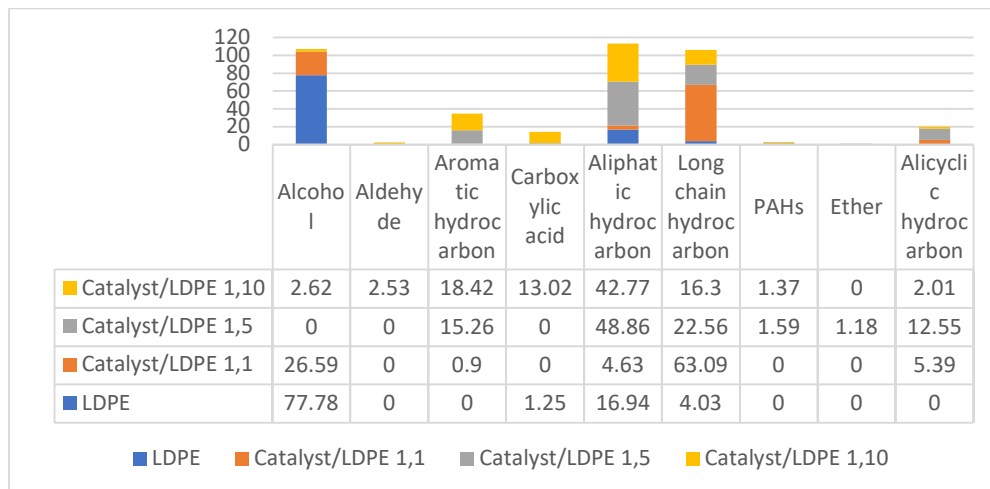


Fig.-5: The Compounds Product Distribution of LDPE Pyrolysis

Prospective and Policy for Reducing Environmental Emission by Pyrolysis of Plastic Waste Using Metal-Activated Carbon

The increasing energy demand has the opposite effect on the availability of fossil energy sources. Fossil energy use, especially in the transportation sector, significantly impacts environmental pollution. Indonesia and several other countries in the world have launched a net zero emission policy in order to restore the earth. One of the embodiments and implementation of this policy is the enactment of an alternative energy mix. Converting alternative fossils into biofuels is a step to support national energy policies and a commitment to reduce global emissions. On the other hand, the use of plastic continues to increase by nearly 200 tons per year, thus harming the increasing accumulation of plastic waste. In 2021, the calculated waste in Indonesia is 68.5 tons, especially from plastic waste reach until 11.6 tons. Plastic material is an essential ingredient in the manufacture of various purposes. The plastic use is increasing because it is considered applicable and relatively cheap. The accumulation of plastic waste, such as LDPE, takes work to handle. Reuse, recycle, and reduce steps have their weaknesses. The government's policy measures to reduce plastic waste need to be supported by strategies, collaboration, and synergy of government, community, and researchers so that the technology for reducing and converting plastic waste can emerge so the community can utilize it. LDPE is produced from petroleum which contains hydrocarbon compounds. The content of polyethylene and hydrocarbons in LDPE makes it easy to convert LDPE into fuel fractions. One way to do this is by catalytic pyrolysis, breaking down polymers to form new compounds

with metal-activated carbon catalyst. Easy, effective, and economical are three critical factors that need to be considered in developing techniques to produce synthetic fuels. Production, sale, and use of plastic from natural resources will generate income from plastic waste by recycling it into energy and turning it into a resource for society. Government policies and regulations regarding using alternative energy and reducing plastic waste must be implemented at the local and national levels. There needs to be an incentive for personal or industrial users of alternative energy and plastic waste processing to reduce pollution and support net zero emission. Technological support such as a promising biomaterial like metal/activated carbon catalyst is also needed so that alternative energy policies and reducing plastic waste can run simultaneously to achieve society's circular economy. This research recommends catalytic pyrolysis with environmentally friendly catalysts, which can add value to plastic waste while reducing energy consumption so that it becomes cleaner production.

CONCLUSION

The Co/activated carbon catalyst from sengon wood waste (*Paraserianthes falcataria*) has been successfully synthesized using carbonization, steam-activation, and wet impregnation methods. This catalyst affects the pyrolysis product of LDPE using a simple-fast method using py-GCMS. The result showed that the quality of activated carbon was 90% close to Indonesian National Standard quality, and metal was successfully loaded into activated carbon with an average crystal size of 0.56nm. The treatment process increases acidity, surface area, pore radius, and pore volume, which leads to increased activity and selectivity of the catalyst. LDPE py-GCMS using Co/activated carbon catalyst 1:5 showed aliphatic, aromatic, and alicyclic hydrocarbon products of 48.86, 15.26, and 12.55%. From the technology perspective, the Co/activated carbon from sengon wood waste has excellent potential to develop for pyrolysis applications.

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CONFLICT OF INTERESTS

The authors declare that there is no conflict of interest in this research and manuscript.

AUTHOR CONTRIBUTIONS

All the authors contributed significantly to this manuscript, participated in reviewing/editing, and approved the final draft for publication. The research profile of the authors can be verified from their ORCID ids, given below:

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