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FORMALDEHYDE RESIN AS A SOLID FUEL AND ACTIVATED CARBON

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This work was aimed to assess the potential of formaldehyde resin residue as a solid fuel and activated carbon. The resin materials were characterized in terms of calorific value, elemental composition, thermal stability, specific surface area, surface side groups, flame retardancy, flue gas and the toxicity characteristic leaching procedure (TCLP). Meanwhile, the hardened resin was chemically activated using potassium hydroxide and phosphoric acid to remove methylene blue. The TCLP shows that resins are stable with minimal leaching of minerals. The resins are composed primarily of carbon with 3.1 % ash content with the high calorific values. The KOH-activated carbon exhibits a maximum dye adsorption capacity of 388 mg/g, surpassing that of H_3PO_4-activated carbon by only 21.2 mg/g. The analysis of hardened resins has revealed its versatility as a solid fuel and activated carbon, thereby supporting sustainability efforts.

Keywords: Activated carbon, calorific value, formaldehyde resin, solid fuel

1. Introduction

Formaldehyde naturally exists as a colorless and flammable gas with a strong smell as well as a boiling point of -19 °C. It is highly soluble in water and commercially available at a concentration of 36 %. Nowadays, solutions of formaldehyde are widely used in making resins as adhesives, paints, lacquers and coatings, essential for manufacturing composite and engineered wood products of household furnishings and structures [1].

In these manufacturing processes, the production of by-products is typically inevitable. One of the most challenging waste management issues concerns the handling of formaldehyde (polymer) resin residue, a by-product of these processes. The material is normally classified as scheduled waste (SW 320) since formaldehyde may remain in the residue, necessitating special disposal by incineration [2].

As the environment worldwide is becoming more sustainable, potential utilizations of this by-product are sought to stimulate a circular economy via a zero waste strategy. Therefore, the present work sought to investigate the physicochemical characteristics of formaldehyde resin residue as a solid fuel and activated carbon, hopefully leading to broad applications in briquette technology and pollution control.

2. Experimental

Two formaldehyde resin materials, namely film resin and hardened resin, were supplied by SF-PG, Malaysia. Methylene blue, potassium hydroxide and phosphoric acid were purchased from HmbG Chemicals (Germany), all of which are of analytical grade.

2.1. Physicochemical characteristics

The calorific value was measured using a bomb calorimeter (IKA C3000) and calculated based on the rise in temperature and the known heat capacity of the calorimeter [3]. The elemental composition of carbon, hydrogen, nitrogen and sulfur in resin materials was measured by an Elementar vario MICRO Cube (Germany).

The hardened resin was dried in an oven at 110 °C for 4 h to determine the moisture content. The thermal stability and ash content were determined by heating the resin materials at 300 and 850 °C in a muffle furnace for 2 to 24 h before the changes in weight were recorded [4].

The thermal decomposition profiles of resin materials were obtained using a thermogravimetric analyzer (PerkinElmer TGA 4000) under a flow of N_2 at a rate of 10 ºC/min from room temperature to 900 ºC.

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Table 1: Calorific values of resin materials

Material	Calorific value (MJ/kg)
Hardened resin	23.6
Film resin	23.7
Heat-treated hardened resin (300 °C)	28.1
Heat-treated film resin (300 °C)	29.3
With H_3PO_4 binder	
Hardened resin	20.8
Film resin	20.0
Heat-treated hardened resin	23.8
Heat-treated film resin	22.2

The resins materials were scanned for surface functional groups using a Fourier transform infrared spectrometer (Spectrum One) from 4000 to 400 cm^{-1} [5].

The toxicity characteristic leaching procedure (TCLP) is a chemical technique to identify hazardous elements present in a material. First, the sample was oven-dried at 60 °C and ground to pass through a 9.5 mm sieve. The extraction solution was determined based on the pH. 1.5 g of material was weighed and mixed with 30 mL of extraction fluid. The mixture was agitated for 18 ± 2 h before filtering the extract and preserving it at $pH < 2$ by adding drops of concentrated HNO_3 prior to taking ICP measurements [6].

2.2. Activated carbon and performance

The hardened resin was subjected to chemical activation to evaluate its viability as a source of activated carbon for treating dye wastewater. Two commonly used activators, namely potassium hydroxide (KOH) and phosphoric acid (H_3PO_4), were employed at a fixed mass ratio of 1:1. Activation was performed under an anoxic environment in a muffle furnace at 600 °C for 2 h.

The activated carbon was characterized for textural properties using a Micromeritics TriStar II Plus at 77 K, the temperature of liquid N_2. The Brunauer-Emmett-Teller (BET) method was used to compute the specific area, mesopore volume and microporosity.

The performance of activated carbon was evaluated by the adsorption of methylene blue. 50 mg of activated carbon was added to 50 mL of methylene blue solution at varying concentrations before being allowed to equilibrate over 5 days. Afterwards, the residual concentration was measured using a visible spectrophotometer at a wavelength of 600 nm. The amount of dye adsorbed was calculated by a mass balance.

2.3. Flame retardancy and flue gas analysis

The resin materials were exposed to a direct fire source for 44 s and the images of flame retardancy captured using a Photron FASTCAM Mini UX50 high-speed camera.

Flue gas analysis was carried out using a testo 350 flue gas analyzer. The resin material was added in a muffle furnace heated under anoxic conditions at 428 °C.

3. Results and discussion

3.1. Physicochemical characteristics

The calorific values of resin materials are summarized in *Table 1*, which range from 23.6 to 29.3 MJ/kg, comparable with typical solid fuels such as anthracite coal and dried firewood with values of 32.5 and 21.7 MJ/kg, respectively. In general, the calorific value increased following heat treatment at 300 °C with some weight loss, indicating the removal of light volatiles (oxygen, hydrogen, etc.). At which point, the carbon content increased, thereby increasing their energy content.

Adding H_3PO_4 as a binder (at 10% by weight) decreased the calorific value. A suitable binder containing a sufficient amount of carbon that grips strongly could be sought to maintain the calorific value.

A considerable weight loss was recorded when the resin materials were heated at high temperatures. The film resin exhibited a greater weight loss due to its brittle structure and highly exposed area compared to the rigid structure of hardened resin. At 300 °C, the weight loss was mainly due to light volatiles, while at 850 °C, was due to fixed carbon and heavy volatiles. The hardened resin is thermally stable with a yield of 12% at 850 °C, suggesting the presence of carbon black. The ash content for both resin samples was 2% after being heated at 850 °C for 24 h. Images of the ash are shown in *Figure 1* and its reddish color indicates that it is rich in iron (Fe).


(a) (b)

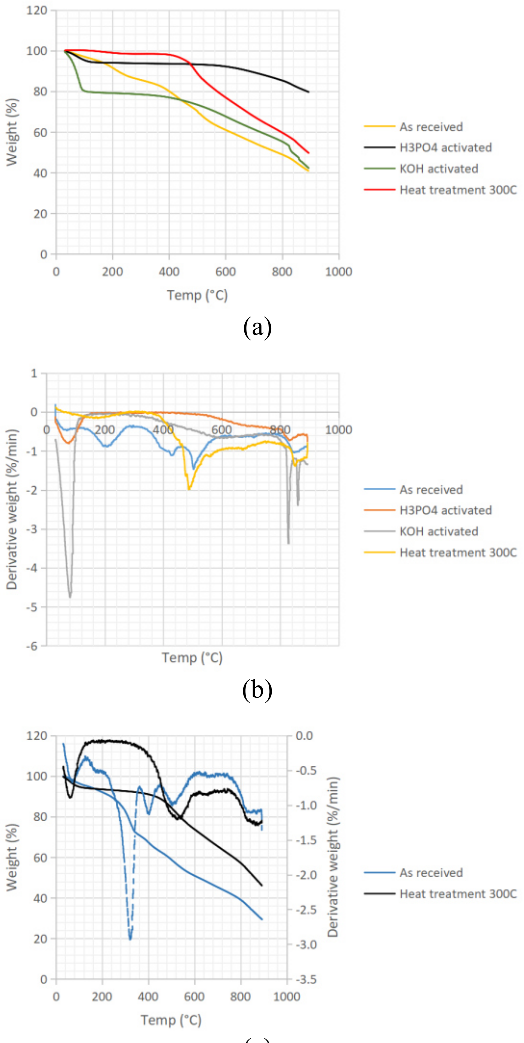
Figure 1: Images of the ash from (a) hardened resin and (b) film resin

Analyzing the solubility of hardened resin in solutions helps to determine its chemical interactions as well as make informed decisions regarding environmental and waste management practices [7]. The moisture content of hardened resin is 7.5%, which is stable in water with no significant weight loss. Nonetheless, some weight loss was detected in KOH (4.3%) and H_3PO_4 (8.2%) solutions during the impregnation process, showing that the light volatiles are soluble in acids and alkalis, thereby vaporizing with water at 110 °C. However, these proportions are relatively small when compared to its moisture content.

Table 2: Elemental composition of resin materials

	N	C	H	S	O*
Hardened resin	1.1	60.8	5.2	0.3	32.6
Hardened resin (Pre-treatment)	0.6	66.2	3.9	0.3	29.0
Film resin	0.3	57.8	5.7	0.3	35.9
Film resin (Pre-treatment)	0.4	73.7	4.5	0.5	20.9
KOH-activated carbon	0.3	60.2	1.0	0.2	38.3
H_3PO_4-activated carbon	0.5	64.7	1.5	0.2	33.1

*Calculated by difference



(a)

(b)

(c)

Figure 2: (a) TGA and (b) DTG profiles of hardened resin materials as well as (c) TGA and DTG profiles of film resin materials

The trend in the weight loss of resin materials when heated is shown in *Figure 2*. The as-received hardened resin exhibited a gradual weight loss as the temperature increased and the remaining weight was 40% of its initial value at 900 °C. Several DTG peaks at 200 °C are attributed to light volatiles, while those between 430 and 500 °C correspond to heavy volatiles [8]. The heat-treated sample is thermally stable up to 430 °C before declining to 50% by 900 °C. Using a simple mass balance, the proportion of light volatiles in hardened resin is about 10%. A sharp peak at 487 °C was attributed to the release of heavy volatiles. The as-received resin and activated samples exhibit a common peak between 80 and 100 °C attributed to the release of moisture. The moisture content of the KOH-activated carbon is greater because of its well-developed porous structure that entraps more moisture from the surroundings [9]. Likewise, it is more susceptible to degrade at high temperatures because of the collapse of its porous structure. From *Figure 2c*, the mass of the as-received film resin gradually decreases with a yield of 29% at 900 °C. Three DTG peaks at 90, 320 and 400-500 °C denote the release of moisture as well as light and heavy volatiles, respectively [10]. Furthermore, no peaks associated with light volatiles are found regarding the heat-treated resin which exhibited a yield of 46% at 900 °C. The proportion of light volatiles in film resin is estimated to be 17%.

The elemental compositions measured are summarized in *Table 2*. Both as-received resin materials contain high carbon contents of about 60% which increased following heat treatment at 300 °C, suggesting the release of light volatiles such as CO and CO_2 as a result of combustion [11]. Accordingly, the calorific value increased. For the samples of activated carbon, the liberation of hydrogen is prevalent, implying the creation of aromatic-graphitic structures.

The FTIR spectra of resin materials are shown in *Figure 3*. All the samples demonstrate similar peaks that correspond to surface functionalities, even after heat treatment (300 °C) and activation (600 °C). The liberation of light volatiles during heat treatment as well as light and heavy ones during activation does not significantly influence the presence of functional groups. Except for KOH-activated carbon, the spectra become simpler as the peak intensities reduce, indicating partial decomposition of functional groups during the activation process [12].

The as-received hardened resin was originally in liquid form but solidified as a result of gelation and as it aged, resembling the resorcinol-formaldehyde (RF) carbon gel process [13]. Resorcinol reacts with formaldehyde to form a hierarchical porous network composed of aggregated particles in the presence of the catalyst K_2CO_3. This reaction is irreversible and the solid formed is thermally stable. The hardened formaldehyde resin used in this work contains both light and heavy volatiles, moreover, can be easily activated using KOH to form porous materials unlike RF carbon gel [13].

The results regarding the leaching of metal elements from hardened resin evaluated by TCLP and XRF are summarized in *Table 3*. The metal elements measured by XRF in the hardened resin and the derived activated carbons are consistent. All samples are rich in Fe displaying elemental compositions of about 90%, except for H_3PO_4-activated carbon that contains 76.7% Fe and a

Table 3: Metal elements in hardened resin materials determined by XRF and their leaching characteristics (TCLP)

Element (ppm)	KOH-activated	H_3PO_4-activated	Hardened resin	TCLP (Hardened resin)
Al	2700	11200	13200	108
Si	15400	67900	33800	134
S	2030	623	2530	6.7
Cl	86	76	332	0
K	12700	0	2050	0
Ca	32000	972	15200	69.4
Ti	3820	1480	12400	0
Fe	905000	767000	882000	0
Zn	8160	4050	1450	0
Sr	87	0	0	0
Zr	7020	7550	10400	587
Sn	28	46	52	0
Eu	1380	0	481	0
Gd	1040	0	0	0
Tb	6420	9020	7910	0
P	0	129000	0	0
Pb	0	170	0	0
Rn	0	42	0	0
As	0	0	43.4	0
Rb	0	0	181	0
Nb	0	0	46.7	0
Au	0	0	284	0

considerable proportion of P deposits, that is, 12.9%, following the use of an activator. All the metals in these samples are naturally occurring or originate from substances used in their production. According to TCLP analysis, the hardened resin is stable as practically no metals leached out from the solid matrix, only 0.01%.

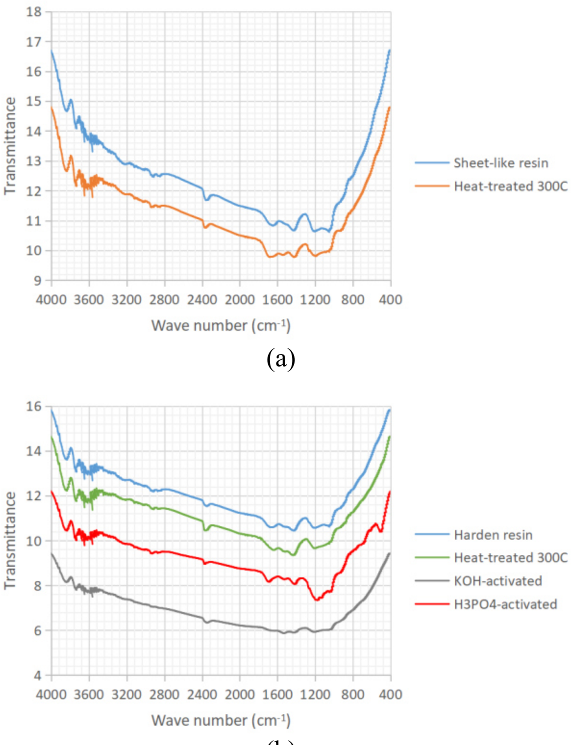
3.2. Activated carbon and the adsorption of dyes

The textural characteristics of types of activated carbon derived from hardened resin and other sources from the literature are summarized in *Table 4* [13]-[14]. The burnout of organic components from resin during pyrolysis resulted in a reduction in mass to 46.8% for KOH-activated carbon and 35.7% for H_3PO_4-activated carbon, usually resulting in a porous structure with altered surface chemistry [13]. The KOH-activated carbon exhibits a greater microporosity of 84%, signifying the effectiveness of KOH as a strong dehydrating agent for pore formation.

Images of the activated carbon of hardened resin are presented in *Figure 4*. The effects of pore formation, namely surface cracks, crevices and multiple open pores, are evident in KOH-activated carbon, while the development of pore channels is not apparent in H_3PO_4-activated carbon.

Table 4: Textural characteristics of the different sources of activated carbon

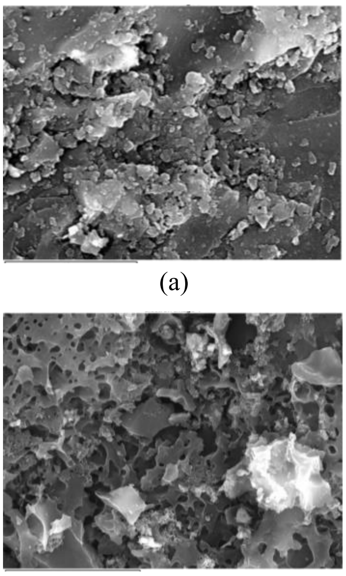
	KOH-activated carbon	H_3PO_4-activated carbon	RF carbon gel [13]	Commercial AC [14]
Yield (%)	46.8	35.7	-	-
pH	8.8	4.8	8.8	-
BET surface area (m^2/g)	661	140	433	909
Methylene blue capacity (mg/g)	388	21.2	135	344
Micropore area (m^2/g)	626	119	358	748
Mesopore area (m^2/g)	35.2	21.3	75	161
Micropore volume (cm^3/g)	0.302	0.06	0.17	0.347
Mesopore volume (cm^3/g)	0.056	0.035	0.09	0.095
Total pore volume (cm^3/g)	0.358	0.095	0.26	0.442
Average pore diameter (nm)	2.2	2.7	2.4	1.9
Micropore content (%)	84	63	65	79



(a)

(b)

Figure 3: The FTIR spectra of (a) film resin and (b) hardened resin materials


(a)

(b)

Figure 4: Images of (a) H_3PO_4-activated carbon and (b) KOH-activated carbon

The initial concentration is one of the critical parameters in the dye adsorption process. The adsorption isotherm of methylene blue onto the activated carbon of hardened resins is shown in *Figure 5*. KOH-activated carbon demonstrates a strong intensity (steep gradient) at low concentrations, signifying a favorable degree of dye removal. Its higher surface area of 661 m^2/g offers more active sites to interact with dye molecules. Accordingly, the maximum capacity of 388 mg/g for KOH-activated carbon is greater than 21 mg/g for H_3PO_4-activated carbon, moreover, the dye adsorption of KOH-activated carbon is superior when compared to RF carbon gel [13] and commercial activated carbon [14].

3.3. Flame retardancy and flue gas analysis

The resin materials were exposed to a direct fire source for 44 s. Images captured using a Photron FASTCAM Mini UX50 high speed camera are shown in *Figure 6*. 14.9 mg of hardened resin was used and a reduction in mass of 13% recorded after heating with no significant changes in its physical appearance. These findings are supported by the TGA profiles at 300 °C in *Figure 2*. Meanwhile, the reduction of mass regarding the film resin of 64% was bigger due to the glowing fire which readily ignites and exhibits a poor flame retardancy due to its sheet-like texture, exposing it more to the heat source.

Table 5: Flue gas composition

Flue gas (ppm)	Film resin	Hardened resin
CO	13678	12476
NO	12	6
NO_2	1.7	0.3
NO_x	1.7	6.3
SO_2	245	170

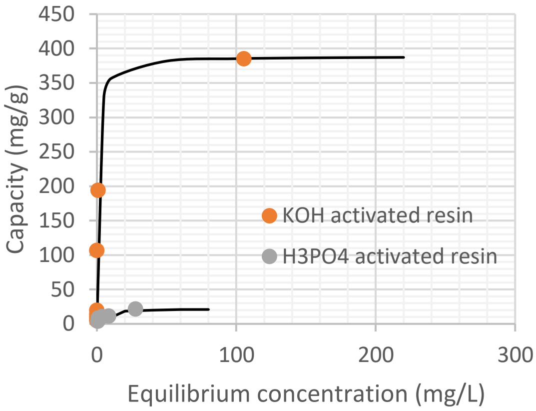
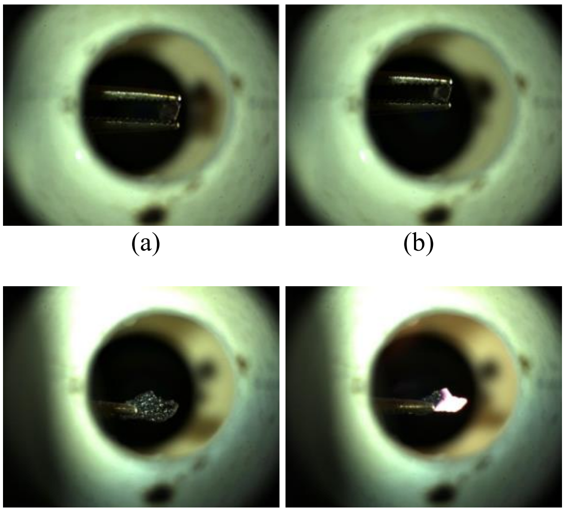


Figure 5: Methylene blue adsorption onto the activated carbon of hardened resins


(a) (b)

(c) (d)

Figure 6: Flame retardancy images of hardened resin ((a) and (b)) and film resin ((c) and (d)); ((a) and (c)) and ((b) and (d)) are images taken before and after heating, respectively

A flue gas analyzer measures and analyzes the composition of gases emitted following combustion, which is essential for monitoring and optimizing the efficiency of combustion to ensure full compliance with environmental regulations [15]-[16]. The results are summarized in *Table 5*. The concentration of CO is high due to an insufficient amount of oxygen for complete combustion inside the furnace. The presence of SO_2 in flue gas is likely because the resin material originally contains 0.3% sulfur (*Table 2*). If applied as a solid fuel, a scrubber can be introduced before exhaust gas from burning the formaldehyde resin is released into the surroundings.

The metal elements in flue gas are presented in *Table 6*. Although iron is a major mineral in resin materials, only trace amounts of it and other metals are detected in flue gas, implying the stability of metals in the resin matrix, which is consistent with the findings from XRF and TCLP in *Table 3*.

4. Conclusions

The TCLP test shows that the hardened resin is a stable material and the metals it contains hardly leach from the solid matrix, moreover, are hardly found in the exhaust stream according to the analysis of the flue gas. The calorific value improves as the carbon content increases following facile heat treatment at 300 °C. When compared with the film resin, the hardened counterpart exhibits promising characteristics as a solid fuel with an energy content of 23.6 MJ/kg as well as activated carbon with a specific surface area of 661 m^2/g and dye capacity of 388 mg/g. The valorization of formaldehyde resin residue will improve waste management, thereby rendering the environment more sustainable.

Table 6: Metal elements in flue gas

Metal (mg/m^3)	Film resin	Hardened resin
Aluminum	0.43	0.17
Calcium	15.34	17.17
Copper	1.37	3.18
Iron	0.32	0.42
Lead	0.09	0.11
Magnesium	1.26	1.31
Nickel	0.09	0.05
Zinc	1.54	2.77

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