CO_2-assisted Low-Temperature Gasification of Petroleum Sludge for Hydrogen Generation using Activated Carbon Catalysts

Behzad Valizadeh, Haneul Shim, Seungje Lee, Young-Kwon Park

School of Environmental Engineering, University of Seoul, Dongdaemun-gu, Seoul 02504, Republic of Korea

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Presenting author email: catalica@uos.ac.kr

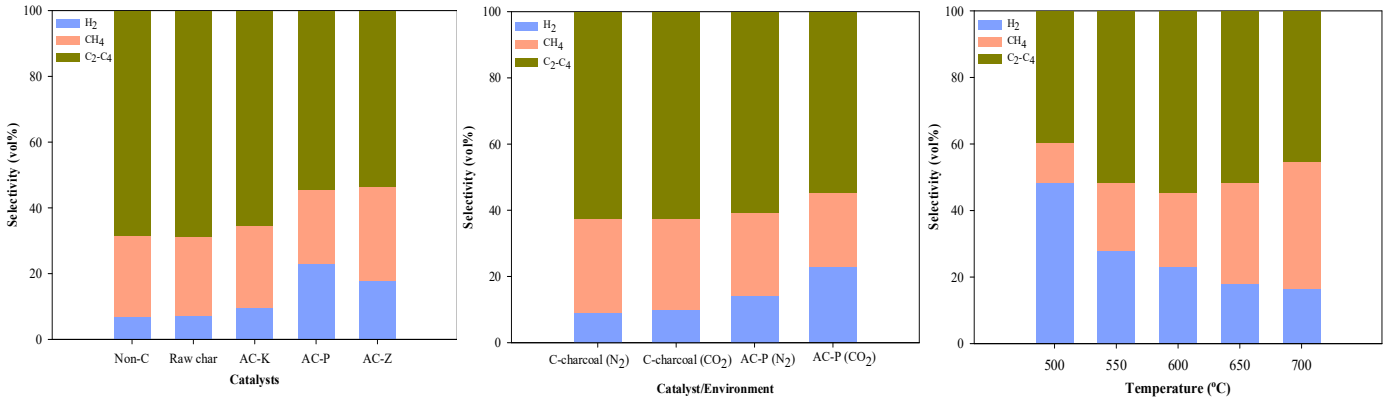
Petroleum sludge (PS) is a hazardous waste extensively produced by various petrochemical industry operations, including mining, refining, and exploitation. The estimated annual worldwide production of PS exceeds 60 million tons, with a cumulative global production surpassing 1 billion tons (Yang et al., 2023). Currently, numerous approaches are employed for PS treatment, including centrifugal separation, solvent extraction, and surfactant-enhanced oil recovery (Johnson & Affam, 2019). Nonetheless, these methods are time-intensive, incur substantial operational expenses, and can lead to environmental pollution. Alternatively, the transformation of PS into valuable fuels not only provides an eco-friendly disposal strategy but also ensures the effective recovery of energy from this waste material to substitute fossil fuels.
Table 1 presents the proximate and ultimate analyses of the parent PS.

Table 1. Proximate and ultimate analyses of PS.

Proximate analysis (%)		Ultimate analysis (%)	
Moisture	19.4	C	82.2
Volatile matter	79.6	H	14.3
Fixed carbon	0.6	N	-
Ash	0.4	O	2.8
		S	0.7

The transformation of PS into hydrogen gas (H_2) through thermochemical conversion technologies has proven to be an effective strategy because H_2 produces only water upon combustion and is a zero-carbon energy source. Notably, the generation of green H_2 from renewable resources is essential for maintaining clean energy characteristics. Gasification stands as an environmentally friendly method to generate H_2-rich gas from PS, which typically takes place in the presence of a gasifying agent (e.g., steam, CO_2, or air) and elevated temperatures ranging from 750 °C to 1500 °C (Venkatachalam et al., 2022). Compared to other thermochemical conversion methods, the gasification approach is highly effective because it captures nearly all the energy while minimizing the generation of harmful substances. Importantly, despite the high temperatures required for gasification, low-temperature gasification (LTG) of PS can further enhance its economic and environmental viability. The use of CO_2 in the LTG (CO_2-assisted LTG) of PS provides a carbon-negative alternative, offers environmentally friendly benefits, and produces more flexible syngas than other gasifying agents (Chan et al., 2021). CO_2 facilitates the thermal decomposition of volatile materials formed during gasification, leading to more effective production of H_2 while suppressing condensable tar. Moreover, CO_2 assists in the cracking of volatile compounds during thermal degradation of manure.
The primary drawback of gasification is significant tar production in the resulting gas, leading to reduced H_2 generation. Thus, catalytic cracking is a viable option for tar reduction and intensifying H_2 production. Carbonaceous catalysts have recently gained increased attention, primarily because of their ability to avoid coke formation.

This study presents a viable solution with the focus on conversion of PS into H_2–rich gas via low-temperature gasification (LTG) using sawdust waste-derived activated carbon catalysts and CO_2 medium. Activated carbon catalysts were prepared using different chemical agents including H_3PO_4 (AC-P), $ZnCl_2$ (AC-Z), and KOH (AC-K) and were compared with commercial charcoal in the LTG of PS. Chemical activation of sawdust showed a considerable enhancement in the physicochemical properties of resulting activated carbons and their catalytic performance, where the H_2 selectivity were differed in the following order; Non-C (6.87 vol%) < raw char (7.10 vol%) < AC-K (9.71 vol%) < AC-Z (17.80 vol%) < AC-P (22.94 vol%) (Figure 1a). These findings are attributed to the promoted chain rupture and dehydrogenation reactions, both of which were stimulated over porous structure and Brønsted acid sites of ACs catalysts and in the presence of CO_2.



(a) (b) (c)

Figure 1. Gas composition from LTG of PS; using different catalysts under CO_2 at 600 °C (a), using C-charcoal and AC-P catalysts under different environments at 600 °C (b), and using AC-P under CO_2 at different temperatures (c).

In addition, the use of AC-P achieved higher gas yield and H_2 selectivity under CO_2 (58.09 wt.% and 22.94 vol%, respectively) than under N_2 (56.83 wt.% and 14.09 vol%, respectively). Also, the employment of AC-P produced more H_2 compared to commercial charcoal under both N_2 and CO_2 environments (Figure 1b). Whereas the yield of gas enhanced by increasing the reaction temperature (68.20 wt.% at 700 oC), H_2 selectivity showed a decent trend with elevating reaction temperature, ranging from 48.41 vol% (at 500 °C) to 16.31 vol% (at 700 °C) (Figure 1c).

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