Exploring the technical and environmental potentialities of rice husk-derived biochar for H_2S removal

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Significance and Relevance

Rice Husk (RH) and biochar were treated with KOH and NaOH before and after pyrolysis at 600 °C under N_2 and CO_2 atmospheres. Alkali pre-activation in CO_2 reduced biochar yield and carbon content but significantly improved specific surface area (SSA) and pore volume (PV), with KOH being more effective than NaOH. The highest SSA and PV (178.4 m^2/g and 0.60 cm^3/g) were achieved with pre-activated KOH-RH in CO_2 (KOH_RH_CO2). H_2S removal tests showed commercial activated carbon (CAC) and KOH_RH_CO2 performed best. At H2S = 35 ppm at GHSV = 3822 h^{-1}, CAC and KOH_RH_CO2 achieved 65.12 and 40.52 mg H_2S/g, with carbon footprints of 0.12 and 0.08 gCO_2eq/g H_2S removed, respectively.

Preferred and 2nd choice for the topic: 1°. Green chemistry and biomass transformation, renewable resources conversion. 2nd Circular economy.
Preferred presentation: Oral preferred or Short Oral

Introduction and Motivations

The Next Generation Level Europe program promotes the green transition by considering renewable energy and waste management. Biogas, produced via anaerobic digestion, is a key renewable energy source but contains toxic H_2S, which must not exceed 5 ppm (WHO). Traditional methods use activated carbon[1], but an alternative can be the biochar produced through slow pyrolysis (sPY) of agricultural waste like rice husk (RH) (European RH production is around 560000 t/y). This study assessed the production and environmental feasibilities of replacing commercial activated carbon with RH-derived biochar as well as activated to remove H_2S by reducing fossil resource consumption, promoting biomethane production, and converting agro-waste into valuable materials.

Materials and Methods

Figure 1 depicts the adopted approach. Pre- and post-activation treatments aimed to enhance biochar's physical and chemical properties. RH was impregnated with KOH or NaOH in a ratio equal to 1:1, before and after pyrolysis at 600°C at 15 °C/min, for 1 h under N_2 or CO_2 atmospheres. The sPY was performed in a fixed-bed reactor and the conditions were based on our previous study[2]. The most promising biochars and commercial activated carbon (CAC) (as a reference), were tested as adsorbents in H_2S dynamic removal tests. These tests were conducted in a vertical fixed-bed reactor at continuous flow, atmospheric pressure, at 25 ± 2 °C, by varying H_2S from 35 to 700 ppm and gas hourly space velocity (GHSV) between 30573 and 3822 h^{-1}. The RH, biochars, and spent biochars were chemically and physically characterized. The biochars with the highest H_2S removal were compared through an ex-ante carbon footprint analysis (CF) (ISO 14067) to identify the best compromise between technical and environmental performances.

Results and Discussion

RH and biochar were activated with KOH and NaOH before and after pyrolysis at 600 °C under N_2 and CO_2 atmospheres. Results indicated that pre-activation with alkalis under CO_2 slightly decreased biochar yield and carbon content, compared to N_2. Alkali pre-activation in CO_2 significantly increased the specific surface area (SSA) and pore volume (PV) of biochars, with KOH more effective than NaOH (Figure 2). Pre- and post-activation with KOH were better than with NaOH, hence H_2S experiments tested: pre-and post-activated biochar with KOH under CO_2, RH-biochar produced under CO_2 and N_2

as a positive control, and commercial activated carbon (CAC) as reference. The performances of these materials were tested at H_2S concentrations of 35 and 70 ppm at three GHSVs: 30573, 15286, and 7643 h^{-1}. Increasing the concentration from 35 to 70 ppm all materials' adsorption capacity and breakthrough time decreased. Additionally, higher GHSV reduced adsorption capacity and breakthrough time. The best performances were observed with CAC and biochar from RH pre-treated with KOH (KOH_RH_CO_2). Hence, these two materials were deeply investigated increasing H_2S concentration from 35 to 700 ppm and decreasing the GHSVs from 7643 to 3822 h^{-1} (Figure2). Higher H_2S concentrations reduced the adsorption capacity for both materials due to faster breakthrough times, caused by a greater concentration gradient and increased mass transfer coefficient. However, lower GHSVs improved adsorption capacity and breakthrough times[3]. The best results were obtained at H_2S = 35 ppm at GHSV = 3822 h^{-1}: CAC and KOH_RH_CO_2 achieved 65.12 and 40.52 mgH_2S/g, respectively. Under these conditions, the CF values for CAC and KOH_RH_CO_2 were 0.08 and 0.12 g CO_2 eq/g H_2S removed, respectively.

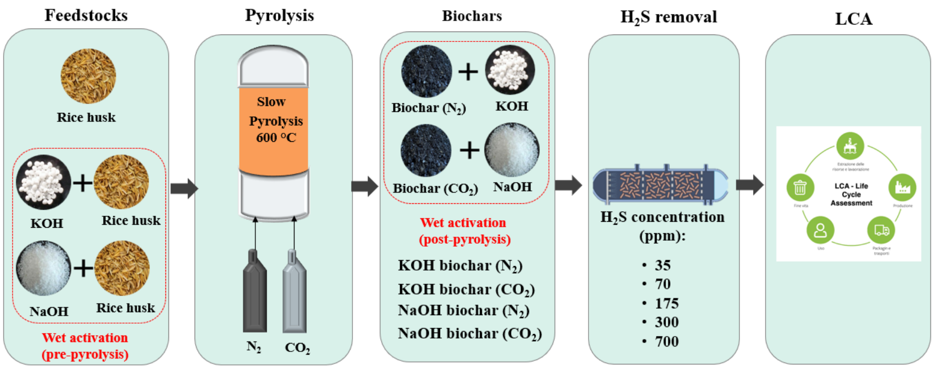

Figure 1: adopted approach to prepare the biochars and test them

	Specific surface area (m^2g^{-1})	Pore volume (cm^3g^{-1})
Without treatment		
Untreated BC (N_2)	55.7	0.018
Untreated BC (CO_2)	141.0	0.084
Pre-pyrolysis activated		
NaOH-BC (N_2)	102.3	0.268
NaOH-BC (CO_2)	123.0	0.255
KOH-BC (N_2)	117.6	0.341
KOH-BC (CO_2)	178.4	0.598
Post-pyrolysis activated		
BC (N_2)-NaOH	68.7	0.127
BC (CO_2)-NaOH	107.6	0.101
BC (N_2)-KOH	99.0	0.197
BC (CO_2)-KOH	152.0	0.311

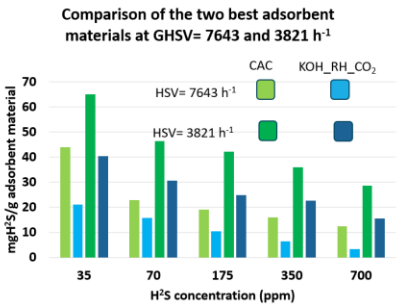

Figure 2: Characterization of adsorbent materials and results of H_2S removal test on the most promising adsorbent materials (commercial activated carbon (CAC) and pre-activated RH with KOH).

References:

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