HYDROTHERMAL CARBONIZATION OF GRAPE SEEDS FOR ADSORBENTS PRODUCTION

Universidad Autónoma de Madrid

Carbon2018

Javier Manzano, John Villamil, Ismael F. Mena, Elena Diaz, Ángel F. Mohedano, Juan J. Rodriguez*

Chemical Engeneering Section, Autonoma University of Madrid (UAM). C/Francisco Tomás y Valiente, 7, 28049 Madrid, Spain.

*email: elena.diaz@uam.es

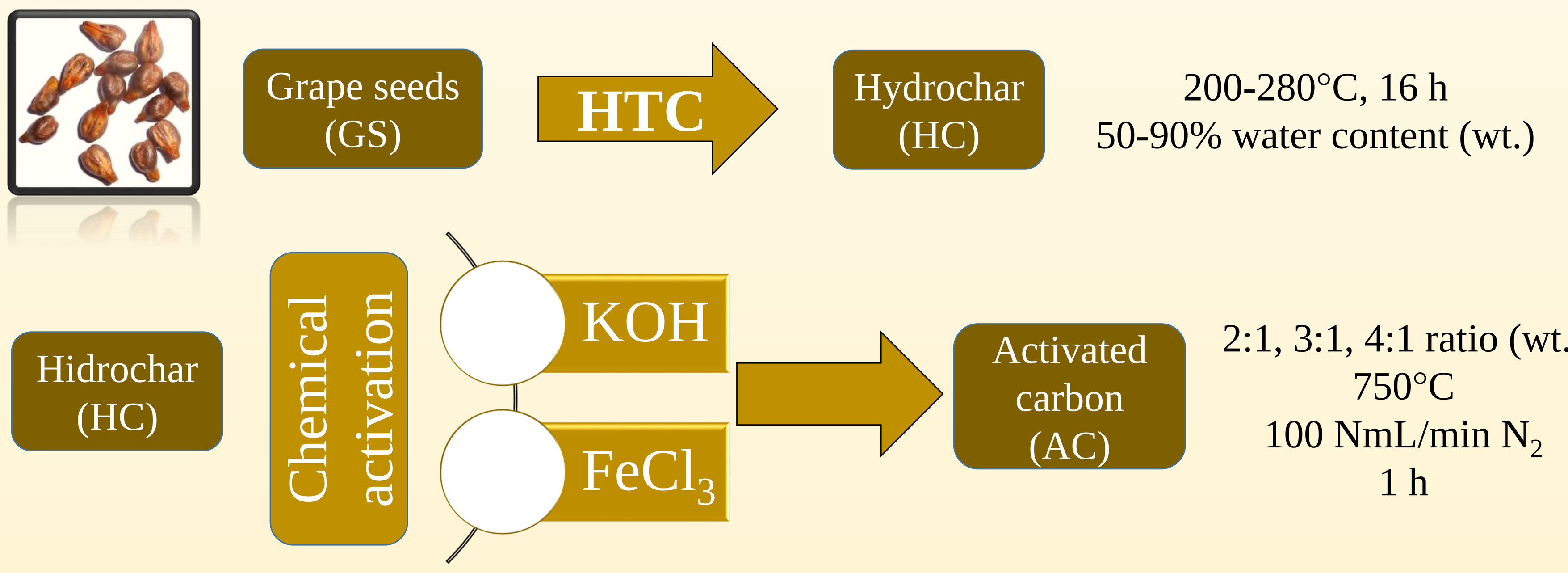
INTRODUCTION

Hydrothermal carbonization (HTC) is becoming an increasingly attractive topic in biomass conversion due to its simplicity, soft operating conditions (temperature and pressure) and the lack of an energy-extensive drying process[1]. The resulting solid product (hydrochar (HC)), presents high carbon content and a relatively high heating heat value (HHV). This material can be used in contaminant remediation, soil amelioration, carbon sequestration, energy storage, and also as a low-cost catalyst support and adsorbent, increasing the porous structure of these materials[2]. For this purpose, the HC is subjected to physical or chemical activation.

The aim of this work is to study the potential of grape seeds as precursor for the production of carbonaceous adsorbents via HTC and chemical activation, analyzing the influence of water content and reaction temperature in HTC process and the role of KOH and $FeCl_3$ as activating agents.

The viability of activated hydrochars as adsorbents has been tested in the removal of 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide ($BmimNTf_2$) ionic liquid from aqueous solution.

MATERIALS AND METHODS



Equilibrium adsorption tests were performed at 20ºC in an orbital shaker. Aqueous solutions (50 mL), from 0 to 5 mmol L^{-1} $BmimNTf_2$, were mixed with the activated carbon (250 mg L^{-1})

RESULTS AND DISCUSSION

HYDROCHAR PRODUCTION

Table 1. Proximate and ultimate analyses of feedstock

Proximate Analysis (db, wt. %)		Ultimate Analysis (db, wt. %)	
Moisture	4.4	C	56.5
Volatile matter	69.9	H	6.6
Fixed Carbon	23.2	N	1.8
Ash	2.3	S	0.1

Table 2. Moisture effect on HTC process (Temperature: 220°C)

Moisture (%)	Yield (%)	C (%)	Fixed Carbon (%)
90	53	70.5	42.1
80	62	70.9	40.1
70	64	71.2	41.2
60	63	70.7	41.4
50	62	69.8	42.1

Table 3. Temperature effect on HTC process (Water content: 60% wt.)

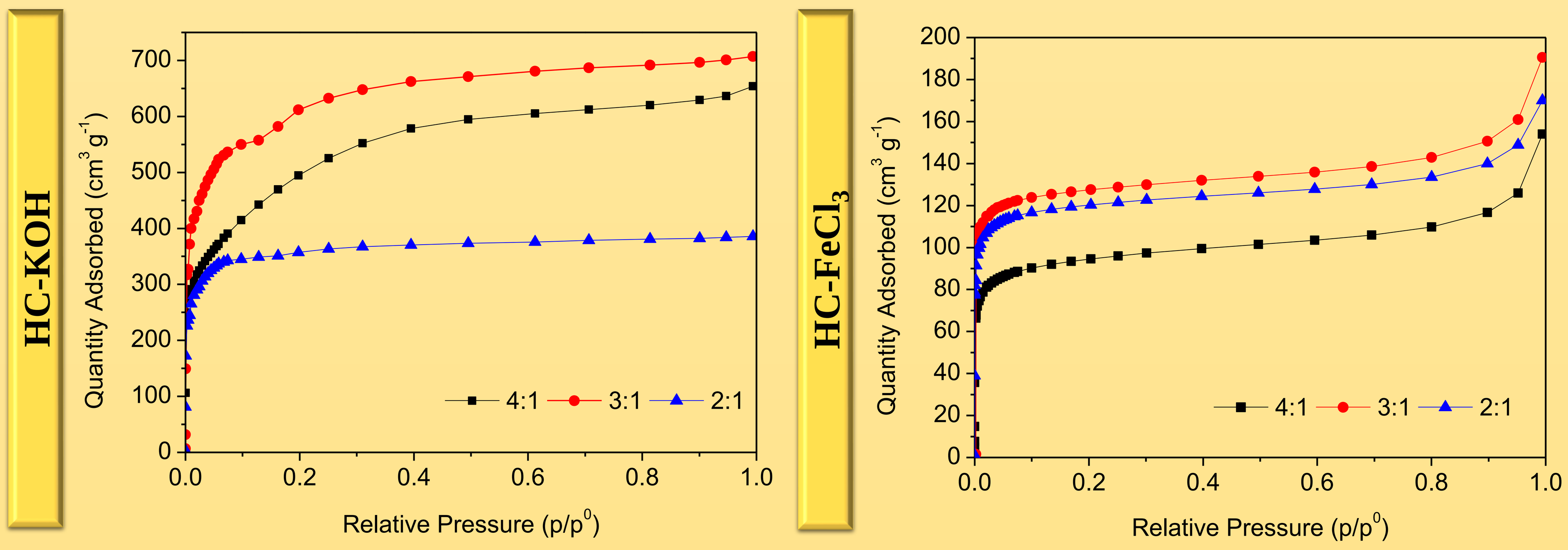
Reaction temperature (°C)	Yield (%)	C (%)	HHV (MJ kg^{-1})
200	77	63.8	26.8
220	59	69.0	27.6
240	59	69.2	29.0
260	63	70.7	30.3
280	62	72.6	30.9

- Moisture in the range studied did not seem to be a determining variable for the HTC process.
- The HHV and carbon content of the HC increased with the temperature, achieving values around 30 MJ kg^{-1} and 71 % wt., respectively, at 260ºC.
- Hydrochar obtained with water content of 60 % was chosen due to the low production of hydrocarbon liquid phase.

ACTIVATED CARBON PRODUCTION

Table 4. Textural properties of activated carbons

Activating reagent	Ratio	A_{BET} (m^2 g^{-1})	S_{micro} (m^2 g^{-1})	V_{micro} (cm^3 g^{-1})	V_{meso} (cm^3 g^{-1})	Average pore diameter (nm)
KOH	2:1	1215	1180	0.74	0.18	2.4
	3:1	2194	2073	0.98	0.05	2.3
	4:1	1780	1520	0.57	0.02	3.0
$FeCl_3$	2:1	394	350	0.12	0.02	5.7
	3:1	417	363	0.17	0.02	6.3
	4:1	312	262	0.17	0.02	5.7

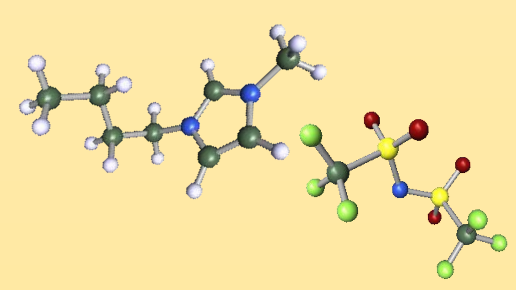


Figures 1 and 2. N_2 adsorption-desorption isotherms of activated carbons

- ACs obtained by KOH activation showed A_{BET} around five times higher than the achieved by $FeCl_3$ activation.
- The HC-KOH materials were mainly microporous and the $FeCl_3$ activation promoted the mesopore development.
- In both cases the best results were obtained with 3:1 ratio.

ADSORPTION TESTS

$BminNTf_2$



1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide

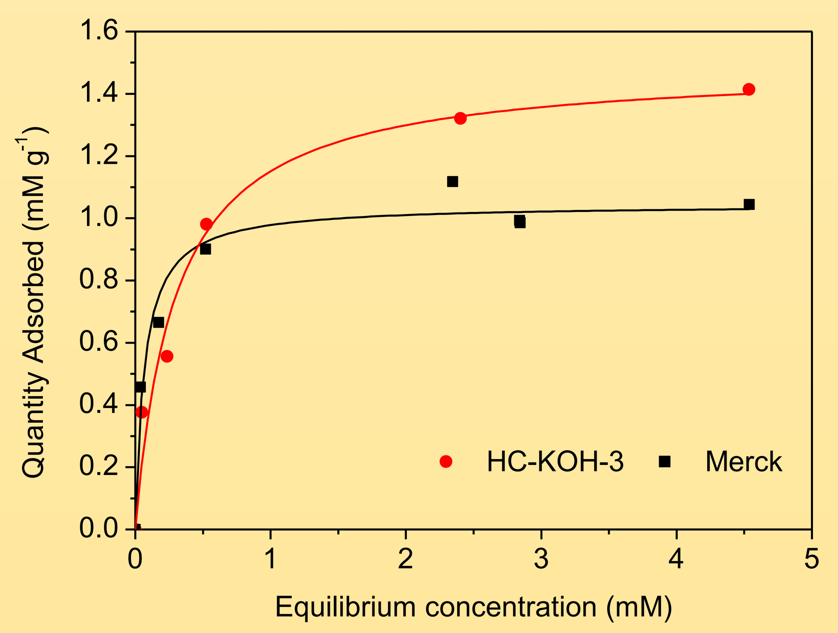


Figure 3. Adsorption isotherms of $BminNTf_2$

Activated Carbon Merck (ACM): A_{BET}: 800 m^2 g^{-1}; V_{micro}: 0.4 cm^3 g^{-1}

The maximum adsorption capacity according Langmuir equation was 1.49 mmol g^{-1} and 1.04 mmol g^{-1} for HC-KOH-3 and ACM, respectively.

CONCLUSIONS

HTC of grape seeds at 260 ºC allowed obtaining and a HC with a carbon content of 70 % wt. and a HHV of 30 MJ kg^{-1} (similar values to vegetal carbon like lignite), which could ready to be used as solid fuel.

Chemical activation of HC with KOH resulted in an activated carbon with high BET surface (2194 m^2 g^{-1}) and higher adsorption capacity of $BmimNTf_2$ ionic liquid than a commercial activated carbon.

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ACKNOWLEDGEMENTS

CTM2016-76564-R (Spanish MINECO), UAM Santander 2017/EEUU/07 and PEJ16/AMB/AI-1327 (Madrid Community)