Catalytic co-pyrolysis of lignocellulose and non-edible vegetable oil using n-ZSM-5: synergistic effects for aromatic hydrocarbons production

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Introduction and Motivations

The catalytic co-pyrolysis of lignocellulose with other H-rich feedstocks is gaining interest as a promising process for the production of biofuels and chemicals, since it may overcome some of the main drawbacks of lignocellulose pyrolysis, such as low yields of aromatic hydrocarbons (AR), fast catalyst deactivation and high bio-oil oxygen content[1]. An acid catalyst is needed to produce a higher quality bio-oil by promoting cracking, deoxygenation, and aromatization of the pyrolysis vapors. In this context, zeolites are the most promising materials to produce AR due to their acidic and textural properties[2]. Plastic residues, waste tires and methane have been investigated for the co-processing with lignocellulose, and synergistic effects have been observed in terms of yield of fuel-grade hydrocarbons[1]. Although the catalytic pyrolysis of lipids is a known and well-studied process to produce AR[3], the literature about the catalytic co-pyrolysis of lignocellulose and vegetable oils employing zeolites as catalyst is very scarce. In this work, a continuous bench-scale reaction system was used to evaluate the synergistic effects arising from the co-processing of these types of feedstocks in terms of AR production and catalyst stability along the time on stream, and to optimize the system by studying different feed ratios and pyrolysis temperatures.

Materials and Methods

Oak tree (Ence, Spain) and Camelina oil (Camelina Company, Spain) were used as feedstocks for the catalytic co-pyrolysis experiments. They were continuously fed into an ex-situ downdraft fixed-bed reactor divided in two sections: pyrolysis and catalytic zones, which were heated independently. Different Oak/Camelina oil (Oak/Cam) mass ratios were studied (1.5, 2.3, 4, and 9), with a total feeding rate of 5 g/h. Two pyrolysis temperatures were studied for the pyrolysis zone of the reactor (350 and 500 °C), while the catalytic one was kept at 450 °C in all cases. A commercial nano crystalline ZSM-5 zeolite (n-ZSM-5) was used as catalyst (see main properties in Table 1), with a fixed loading of 3 g. The total duration of the runs was 4 h, with bio-oil and gas sampling every hour to monitor their yield and composition over time.

Table 1. Physico-chemical properties of the n-ZSM-5 catalyst.

Sample	Si/Al[a]	S_{BET}[b]	S_{MICRO}[b]	V_{TOT}[b]	V_{MICRO}[b]	$C_{BRONSTED}$[c]	C_{LEWIS}[c]
	mol	$m^2.g^{-1}$	$m^2.g^{-1}$	cc/g	cc/g	mmol/g	mmol/g
n-ZSM-5	50	366	274	0.458	0.171	0.252	0.034

[a] from ICP; [b] from Ar-isotherm at 87 K; [c] FT-IR/pyridine adsorption-desorption (150 °C).

Results and Discussion

As shown in Figure 1.A, the overall bio-oil yield (mean of 4 h of reaction) increases with the amount of camelina oil introduced in the feedstock. In all cases, this bio-oil is rich in AR compounds (mainly in xylene, toluene, benzene, and naphthalene) due to the aromatization activity and shape selectivity provided by the n-ZSM-5 catalyst. However, the pyrolysis of lignocellulose also produces heavy phenolic compounds and other oxygenated hydrocarbons which reduce the bio-oil quality and catalyst stability. Thus, the co-processing of oak with camelina oil leads to a 60% of reduction in the bio-oil oxygen content (Figure 1.A) and a 20% of improvement in the carbon yield of aromatic hydrocarbons referred to both feedstocks ($AR\text{-}C_F$ yield) (Figure 1.B) compared to the additive results calculated as the weighted yields obtained from the pyrolysis of the individual feedstocks (indicated as "Calc."). These results indicate the occurrence of a significant synergistic effect due to the ability of the vegetable oil vapors to act as H donor, thus promoting the deoxygenation of lignocellulose molecules. On the other hand, the increased concentration of olefins from the cracking of the vegetable oil enhances the extension of Diels-Alder condensation reactions with furans[4] produced from lignocellulose, resulting in a highly deoxygenated liquid product with an AR concentration higher than 90 wt%. However, the intensity of the synergistic effect is minimally affected by the feeding ratio, suggesting the presence of a limiting factor such as the availability of reactants, especially furans, or the saturation of the catalyst active sites. However, this result could be a positive feature as it would offer flexibility in terms of process design based on feedstocks availability, prices, and target production volume.

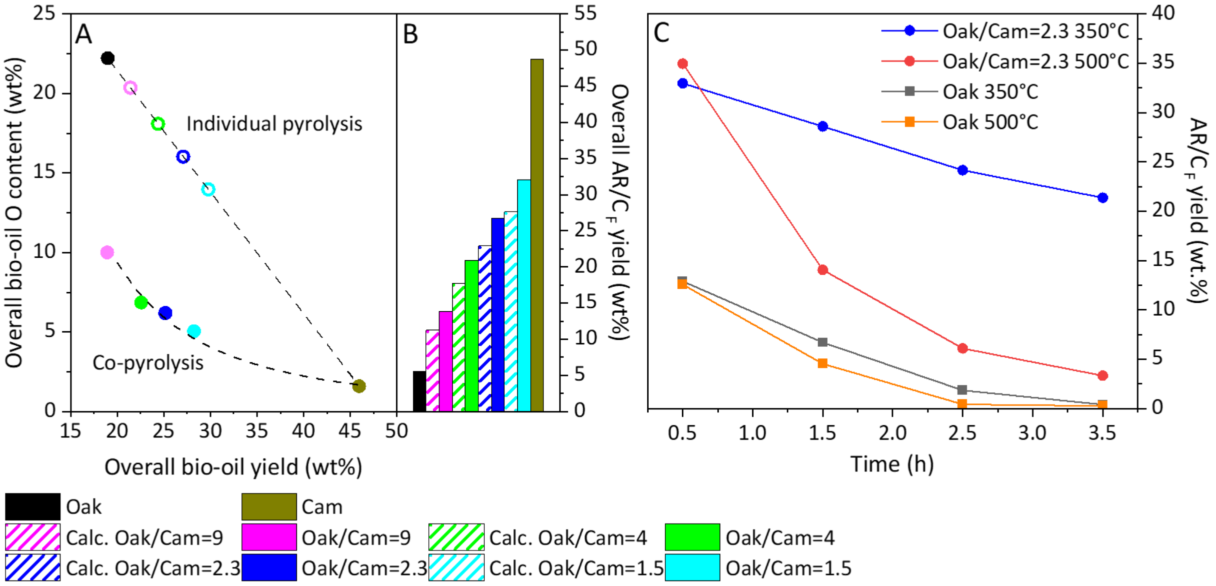

Figure 1. (A) Overall bio-oil mass yield vs O content at different Oak/Cam ratios. (B) Overall AR-C_F yields at different Oak/Cam ratios. (C) AR/C_F yield vs time on stream for oak pyrolysis and co-pyrolysis at different reactor pyrolysis zone temperatures.

On the other hand, the temperature of the pyrolysis zone of the reactor strongly influences the extent of the synergistic effect. Thus, the catalyst stability is sharply improved when working at a relatively low temperature (350 °C) under co-pyrolysis conditions, as shown in Figure 1.C, while only a slight difference between the two temperatures can be observed when processing oak biomass alone. A higher temperature favors the release of lignin oligomers and other oxygenated derivatives, which are known to be major coke precursors. These species competitively occupy the zeolite acid sites and promote secondary reactions that reduce both the selectivity to AR and the zeolite lifetime by blocking its pores[5]. Thus, the zeolite benefits derived from the synergy are strongly enhanced when combined with a low temperature pyrolysis of the lignocellulose.

References

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