

Coupled effect of torrefaction and blending on chlorine removal

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Abstract:

Thailand is an agriculture-based country. It produces large amounts of open burned agricultural residues. A strategy to use them as biofuel all year round is to enhance their fuel properties by coupling blending and thermochemical pre-treatment. In this study, the pyrolytic behaviour of major residues (napier grass, rice straw, cassava stalks and corn cob) exposed to a high torrefaction temperature (300°C) was investigated for various blending ratios, i.e. 100:0, 50:50 and 70:30. The release of chlorine was quantified for each biomass blend, including, a new fouling risk index ratio. Raw biomasses and untreated biomass blends were found to be less suitable as biofuel than torrefied biomasses. The ratio $K_2O:SiO_2$, indicator of fouling risk during combustion, was found to be low for all torrefied blends. The HHV:Cl ratio, indicator of combustion quality, indicated that NG mixed with RS (50:50 proportion) is the most promising blend. Significant synergetic effects were observed for biomasses mixed before torrefaction.

Keywords: Torrefaction; Crop residues; Biomass; Blending

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1. Introduction

Thailand is an agriculture-based country rich in biomass resources. Around ten millions tons of agriculture waste and residues are generated every year and represents a high potential as fuels for power plants. However, the industry is still facing challenges to manage these wastes because of their limitations as fuel, including: 1) not available throughout the year, 2) ash content higher than woody biomass with high chlorine content resulting in operational problems including deposit formation and boiler corrosion during combustion (Kassman et al., 2013). One of the strategies to enhance fuel properties of agricultural waste and limit deposition, slagging, fouling and corrosion in thermal fuel conversion systems is to apply torrefaction (Starfelt et al., 2015). Torrefaction, as a moderate thermal treatment at temperatures ranging from ~200 to 300°C in an inert atmosphere (Bach et al., 2017), transforms biomass properties close to those of fossil coal. Another significant observation is that torrefaction reduces the chlorine content of biomass. The direct co-combustion plants operate generally with a blend containing a maximum of 5-10% biomass. New coal-fired power plants are designed for high co-firing ratios of lignocellulosic biomass, much more than 40% with torrefied biomass without decreasing of energy efficiency and fluctuation of boiler load (Li et al., 2012). The reactivity of blend containing lignocellulosic biomasses was found similar to that of lignite (Toptas et al., 2015). It is clear that using torrefied agricultural residues and their blends is a very effective and sustainable innovative way to dispose waste materials throughout the year. Many studies have focused on improved physicochemical properties of torrefied woody biomass but few on blends of agriculture crops. The first objective of this study is to investigate the torrefaction at high temperature (300°C) of agricultural residues and their blends. The second objective is to quantify the release of chlorine from individual and blended biomasses exposed to the same torrefaction conditions.

2. Material and methods

The four biomasses, including rice straw (RS), napier grass (NG), corn cob (Co) and cassava stalks (Ca) that were used in this study represent major crops in Thailand. All the samples were dried and sieved to a particle size of around 0.5-2 mm for the torrefaction test. The biomass blends were

prepared by physical mixing grinded biomass in the proportion of 50:50 and 70:30 before and after torrefaction. When the ratio is equal to 100%, it means that raw biomass alone was tested. Napier grass has the highest chlorine content, therefore this study focused on blending this biomass material with the three other residues successively. Experiments were conducted in a horizontal quartz tube reactor and a thermogravimetric analyser. About 1.5-2.5 g of sample was placed in an alumina boat located in the quartz reactor, heated to the desired temperature (300°C). Assessment of chlorine content was performed by X-ray fluorescence (XRF) spectrometry, a rapid method used to determine the composition of biomass ash (Xing et al., 2016). The elemental analysis was analysed by use of an elemental analyser (Thermo FlashEA 1112). A number of equations have been published that relate the elemental composition to the higher heating value (HHV) of coal, biomass and municipal waste (Friedl et al., 2005).

3. Fouling risk index and chlorine release

The physical and chemical properties of raw and blended biomasses (untreated and torrefied) are presented in Table 1. Many biomass fuels lead to slagging and fouling in the boiler. A fouling risk ratio $K_2O:SiO_2$ was adapted based on information from the literature to determine which biofuel requires special precautions to avoid fouling problems (Hustad and Barrio, 2000). Lower this ratio, more precautions must be taken to avoid erosion which can occur from higher silica content. All torrefied blends were found to have lower $K_2O:SiO_2$ ratio than untreated ones. This is mainly due to the increase in inorganic elements after torrefaction. NG blended with RS at a 50:50 ratio presented the lowest combustion properties (0.6). When increasing the blending ratio to 70:30, the fuel ratio decreased due to the ash composition of NG which is richer in SiO_2 . A dilution phenomenon of inorganics was therefore observed when mixing biomasses.

Table 1 The physical and chemical properties of raw and blended biomasses
d.a.f = dry ash free, Tor.= torrefied

| Materials | | HHV Mj Kg ⁻¹ | Ultimate analysis (wt%, d.a.f.) | | | | Chemical analysis (wt%, d.a.f) | | | |
|-----------|------|----------------------------|---------------------------------|---|---|----|--------------------------------|------------------|-----------------------------------|-------|
| | | | C | H | N | O | SiO ₂ | K ₂ O | K ₂ O:SiO ₂ | Cl |
| NG | Raw | 16.53 | 41 | 6 | 1 | 52 | 10.94 | 50.22 | 4.59 | 13.54 |
| | Tor. | 23.68 | 56 | 7 | 2 | 35 | 11.91 | 51.26 | 4.30 | 12.56 |
| RS | Raw | 16.93 | 41 | 7 | 1 | 50 | 27.61 | 38.57 | 1.40 | 7.22 |
| | Tor. | 21.31 | 52 | 7 | 1 | 40 | 28.78 | 41.03 | 1.43 | 5.93 |
| Ca | Raw | 15.05 | 37 | 7 | 1 | 55 | 4.17 | 31.65 | 7.59 | 3.31 |
| | Tor. | 24.93 | 57 | 9 | 2 | 32 | 3.03 | 36.82 | 12.16 | 1.66 |
| Co | Raw | 16.12 | 40 | 7 | 2 | 52 | 8.45 | 41.42 | 4.90 | 4.90 |
| | Tor. | 24.85 | 57 | 9 | 1 | 33 | 9.95 | 52.22 | 5.25 | 1.95 |
| NG50RS50 | Raw | 16.88 | 42 | 6 | 1 | 51 | 19.28 | 44.40 | 2.30 | 10.38 |
| | Tor. | 28.74 | 64 | 8 | 2 | 26 | 49.82 | 29.20 | 0.59 | 4.57 |
| NG70RS30 | Raw | 16.59 | 41 | 6 | 1 | 51 | 15.94 | 46.73 | 2.93 | 11.65 |
| | Tor. | 27.26 | 62 | 8 | 2 | 28 | 43.58 | 31.95 | 0.73 | 5.67 |
| NG50Ca50 | Raw | 15.91 | 39 | 5 | 2 | 54 | 7.56 | 40.94 | 5.42 | 8.43 |
| | Tor. | 26.72 | 61 | 8 | 2 | 29 | 24.40 | 35.15 | 1.44 | 4.69 |
| NG70Ca30 | Raw | 16.66 | 41 | 6 | 2 | 51 | 8.91 | 44.65 | 5.01 | 10.47 |
| | Tor. | 27.85 | 63 | 8 | 3 | 26 | 29.52 | 34.75 | 1.18 | 5.93 |
| NG50Co50 | Raw | 16.89 | 42 | 6 | 2 | 59 | 9.69 | 45.82 | 4.73 | 9.22 |
| | Tor. | 24.77 | 59 | 7 | 2 | 32 | 30.71 | 39.33 | 1.28 | 6.03 |
| NG70Co30 | Raw | 16.89 | 42 | 6 | 2 | 50 | 10.19 | 47.58 | 4.67 | 10.95 |
| | Tor. | 26.49 | 60 | 8 | 2 | 29 | 31.51 | 38.45 | 1.22 | 6.72 |

Fig. 1 shows the evolution of heating value versus chlorine content for all raw and blended biomasses torrefied at 300°C. It was observed that there were no significant differences in HHV between the biochars produced from the different biomass feedstocks as well as no significant differences between the individual feedstocks and corresponding blends. All raw and blended

untreated biomasses presented similar heating values at around 16 MJ kg^{-1} whichever the blending ratio applied. This can be explained by the elemental composition of the parent biomasses which are roughly similar. These observations indicate that torrefaction temperature and feedstock type do not significantly affect biochar elemental composition, MC, and HHV corroborated by a recent study (Wei et al., 2016). One observed cassava was the most sensible to the heat treatment increasing the HHV up to 25 MJ kg^{-1} while RS presented the lower value (21 MJ kg^{-1}) validating the EF values calculated in . After torrefaction, HHV was found to range from 24 to 28 MJ kg^{-1} for all blends. The maximum was for NG and RS (50:50). All biomass groups showed a similar trend with a decreasing content in chlorine. From the perspective of different biomass types (raw and blended), the amount of chlorine compounds varied from 3.3 to 13.5% before torrefaction and from 1.6 to 12.5% after torrefaction. A slight decrease was observed for NG while the three other biomasses showed a more emphasised mitigation in chlorine concentration. These results are consistent with earlier findings concluding that approximately 70% of chlorine is released at 350°C with no further release at 500°C (Saleh et al., 2014).

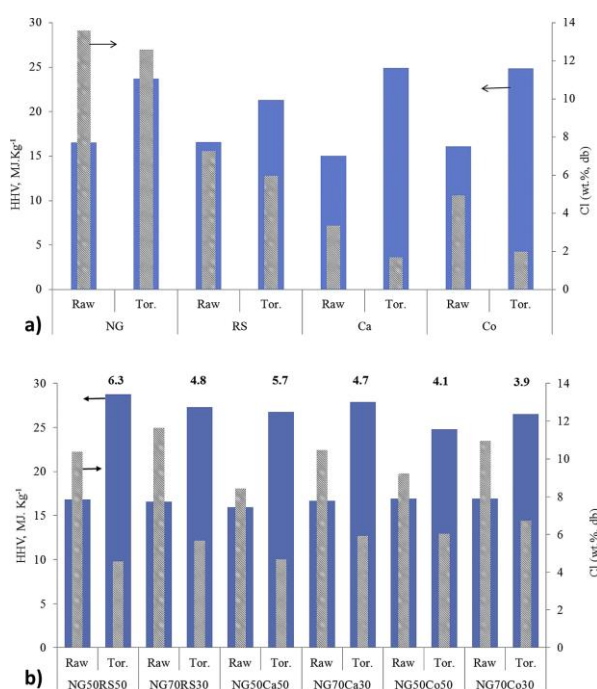


Fig. 1 a) HHV vs Cl content for all biomasses before (Raw) and after torrefaction (Tor.) at 300°C .
b) HHV vs Cl content for all blends before (raw) and after torrefaction (Tor.) at 300°C . The calculated HHV:Cl values are shown in bold. NG ¼ Napier grass; RS ¼ Rice straw; Ca ¼ Cassava stalks; Co ¼ Corn cob.

In terms of combustion, torrefied Ca is the most advantageous biofuel as characterised by the highest heating value (25 MJ kg^{-1}) coupled with the lowest amount of chlorine (1.6%) contributing thereby to minimising slagging and fouling issues. A HHV:Cl ratio was therefore established in this work to provide information about the quality of various biomass blends as biofuel and also some qualitative insights about biomass combustion. The higher the ratio, the better the combustion properties. As shown previously, NG mixed with Ca (NG50Ca50) was expected to be the most promising biofuel (with a ratio of 5.7). However, when NG was blended with RS (NG50RS50), a higher ratio was obtained (6.3). NG70Co30 was found to have a lower ratio (3.9). These results allow us to conclude that the mixing and torrefaction of two biomasses with high chlorine content and low energy density contribute to improve significantly the combustion properties of the blend. The yields of torrefied biomass were found to be almost similar ranging from 56 to 59% and 53-

57% for raw and blend respectively. Torrefied cassava showed the highest energy yield with 95% and half of chlorine was released when RS showed the lowest energy (76%) and lowest chlorine reduction (18%). According to these, NG blended with Ca (50:50) was the least reactive to temperature and presented the highest solid and energy yield with 56.7 and 95.3% respectively while chlorine content was reduced by 44%. The greatest reduction in chlorine content was observed for the blend NG50RS50 with 56% reducing.

4. Conclusion

This study investigated the pyrolytic behaviour and quantified the chlorine release of blended agriculture residues and their parents exposed to a high torrefaction temperature (300°C) performed in a thermogravimetric balance (microparticle) and a batch reactor (macroparticle). The $K_2O:SiO_2$ which is the fouling risk index determining if biofuel require special precautions to avoid fouling problems, was lower for torrefied biomasses compared to untreated blends. The greatest chlorine content mitigation was observed for the mix of napier grass and rice straw with 56% decrease. The HHV: Cl ratio, an indicator of combustion quality, showed that napier grass mixed with rice straw in 50:50 proportion was the most promising blend with the highest ratio (6.3).

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