Compositional modification of products from Co-Pyrolysis of chicken manure and biomass by shifting carbon distribution from pyrolytic oil to syngas using CO₂

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Co-pyrolysis of chicken manure and biomass was investigated in this study. The pyrolysis of individual samples was characterized by thermogravimetric analysis (TGA) under N₂ and CO₂ atmospheres. This demonstrated that the impact of CO₂ content on the physical aspects of pyrolysis such as onset and end temperatures, and residual mass was negligible. However, a high CaCO₃ content (17 wt%) in chicken manure catalyzed the Boudouard reaction. Despite its negligible physical influence, CO₂ evidently affected the co-pyrolysis of chicken manure and biomass chemically. It expedited the thermal cracking of hydrocarbons from the co-pyrolysis of chicken manure and biomass. Moreover, between 550 and 660 °C, CO₂ reacted with condensable hydrocarbons, effectively improving CO generation. This observation suggested that CO₂ acted as both carbon scavenger and oxygen donor in the co-pyrolysis of chicken manure and biomass chemically. It expedited the thermal cracking of hydrocarbons from the co-pyrolysis of chicken manure and biomass. Moreover, between 550 and 660 °C, CO₂ reacted with condensable hydrocarbons, effectively improving CO generation. This observation suggested that CO₂ acted as both carbon scavenger and oxygen donor in the co-pyrolysis of chicken manure and biomass, a driving force for shifting carbon distribution between pyrogenic products. For example, pyrolytic oil was transformed into syngas, especially CO, offering an innovative means to modify compositions of pyrolytic products. These effects were not observed in the presence of CaCO₃ and/or CaO.

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1. Introduction

Over the last decades, global energy production has increased by 150%, equivalent to 13.7 billion tons of petro-oil [1]. However, the major resources utilized in chemical and energy sectors were unchanged, still relying on fossil fuels for 80% of global energy production [2]. This heavy dependence on fossil resources has triggered severe socio-economic problems like energy insecurity due to limited and unevenly distributed natural resources [3–5]. In addition, it drives the perturbation of natural carbon cycle and harms the environment [6,7]. The massive carbon output from anthropogenic activities is overwhelming our ecosystem. Greenhouse gases and particulate matters from complete and/or incomplete combustion processes have been recognized as a crucial factor for triggering global warming [8–10]. To cope with socio-economic and environmental issues stated above, renewable and sustainable energy sources as an alternative to fossil-derived fuel has been extensively developed [11,12]. Among these, biofuels are viable options owing to their intrinsic carbon neutrality [13–15]. In addition, their high content of oxygen offers a better oxidation performance, which reduces the generation of air pollutants such as particulate matter. Furthermore, the mandatory use of biofuels has been politically supported by legislated renewable portfolio standard (RPS) and renewable fuel standard (RFS), which expedites the expansion of biofuels [16,17]. Biofuels are advantageous because they can utilize the pre-existing distribution network without engine modification [18,19].

The first generation of biofuel that is converted from edible biomass has been commercialized. However, its expansion resulted in unexpected side effects (i.e., ethical dilemma, crop price increase, and water shortage) [20,21]. To abate these problems, second (i.e., biofuels from inedible biomass) and third generations (i.e. biofuels

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from aquatic biomass) of biofuels have been investigated over the last decade [22,23]. Despite technical advances, the processes for biofuel production has not yet been commercialized due to their technical inadequacies [24]. The insecure supply chain for biomass due to the regional and seasonal restrictions has been regarded as one of the demerits [25,26]. Therefore, alternative biomasses as raw materials to produce biofuels are in demand. Municipal solid waste (MSW) and agricultural waste [27] such as livestock manure are viable options. The establishment of concentrated animal feeding operations (CAFOs) leads to massive generation of livestock wastes and manures [28,29]. Animal wastes are normally used as an effective fertilizer via composting process [30,31]. However, the surplus of livestock manure, which assimilated nutrients like nitrogen, phosphorous and potassium, resulted in unwanted eutrophication that damaged plants by disrupting the absorbance of other nutrients [32]. In response, anaerobic digestion (AD) has been employed to dispose animal wastes [33]. However, biogas from the AD process requires rigorous purification and extensive concentration steps because of its high content of CO2 (50–60%) [34]. Moreover, one of the crucial steps in the AD process generates sludge. Hence, a method for sludge disposal is required [35]. Thus, biofuel processing technologies to resolve all these demerits are greatly desired.

Thermo-chemical treatments (i.e., pyrolysis and gasification) of manure have potential applications in fuel processing technology, as it could be applied to most carbonaceous materials, insensitive of biomass type [36]. The syngas from the thermo-chemical processes contributes to energy density and can be used as initial feedstock for synthesizing fuels (e.g., ethanol, gasoline, kerosene, diesel, and jet fuel) and chemicals [37,38].

Despite their several technical advantages, the thermo-chemical processes are energy intensive. Thus, a new way to increase their efficiency and modify their products without catalysis is demanded. To further promote sustainability, CO2 can be used in jet fuel) and chemicals [37,38].


developed using a micro gas chromatograph (GC, INFICON) calibrated with a standard gas mixture (RIGAS). The collected condensable hydrocarbons (tar) were quantitatively identified using a GC/TOF-MS system (Agilent 7890/ALMSICO) equipped with an Agilent HP-5MS (60 m x 0.25 mm x 0.25 μm) column. Prior to the analysis, the tars were diluted by 20-fold with dichloromethane (Sigma-Aldrich). All experiments were triplicated to ensure reproducibility.

3. Results and discussion

3.1. Thermolysis of chicken manure under N2 atmosphere

Representative mass decay thermogram and its thermal degradation rate, depicted as differential thermogram (DTG), were incorporated and plotted in Fig. 1(a) and (b), respectively. Disregarding moisture vaporization, Fig. 1(a) shows that mass decay in the thermolysis of chicken manure occurred in three parts: between 210 and 505 °C, 620 and 740 °C, and 760 and 860 °C. The first mass change from 210 to 505 °C indicates the thermal decomposition of organic mass fraction in chicken manure, which is roughly equivalent to 55 wt%. The second mass loss between 620 and 760 °C is roughly equivalent to 30 wt%. The second mass loss between 760 and 860 °C is difficult to describe by TGA. Thus, the chicken manure sample was washed with HCl. Interestingly, significant amount of

Table 1
Proximate analysis of the chicken manure and biomass samples.

<table>
<thead>
<tr>
<th>Component</th>
<th>Chicken manure, [wt. %]</th>
<th>Lignocellulosic biomass, [wt.%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moisture</td>
<td>4.35 (±0.21)</td>
<td>3.34 (±0.19)</td>
</tr>
<tr>
<td>Volatile matter</td>
<td>71.45 (±1.31)</td>
<td>94.78 (±2.11)</td>
</tr>
<tr>
<td>Fixed carbon</td>
<td>7.83 (±0.36)</td>
<td>1.46 (±0.06)</td>
</tr>
<tr>
<td>Ash</td>
<td>16.38 (±0.68)</td>
<td>0.43 (±0.02)</td>
</tr>
</tbody>
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