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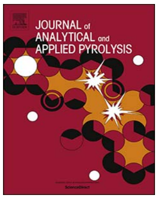

Microwave-assisted catalytic fast co-pyrolysis of *Ageratina adenophora* and kerogen with CaO and ZSM-5

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ABSTRACT

Microwave-assisted catalytic fast pyrolysis (MACFP) of *Ageratina adenophora*, kerogen and their mixtures with CaO and ZSM-5 catalysts are implemented in a microwave-induced reactor. The effects of reaction temperature and CaO/ZSM-5 mass ratio on pyrolysis product yields and selectivities of MACFP of pure *Ageratina adenophora* and kerogen are investigated. A maximum carbon yield of petrochemicals (aromatics + C_2-C_4 olefins + C_5 compounds) from *Ageratina adenophora* of 21.9% is obtained at a temperature of 550 °C and CaO/ZSM-5 mass ratio of 1:3. A maximum petrochemical yield from kerogen of 54.8% is obtained at a temperature of 650 °C and CaO/ZSM-5 mass ratio of 1:3. Likewise, the MACFP of *Ageratina adenophora* and kerogen mixtures is conducted and the effects of reaction temperature and overall effective hydrogen index (EHI) of feedstock are studied. The highest carbon yield of petrochemicals from *Ageratina adenophora* and kerogen mixtures is gained at a temperature of 600 °C. Additionally, it is observed that co-feeding *Ageratina adenophora* with kerogen can facilitate hydrocarbon production and thus show a postive synergy. The carbon yield of petrochemicals from co-feeding is higher than running these two feedstocks under their respective optimal reaction temperatures when EHI is at the range of 0.4–1.0. Besides, coke formation can be inhibited during catalytic co-feeding pyrolysis. These findings from this study pave a new route for biorefinery industries to produce developed products from *Ageratina adenophora* and kerogen through microwave-induced technologies.

1. Introduction

Ageratina adenophora (syn. *Eupatorium adenophorum*) (Asterales: Asteraceae), also commonly known as Crofton weed, sticky snakeroot or Mexican devil, is a weedy perennial shrub originated from Mexico and Central America, and actually it is an alien invasive species that has naturalized and spread into many tropical and subtropical areas worldwide, including Asian, Australian, African and American countries [1,2]. As an invasive plant, *Ageratina adenophora* can trigger negative transformation of ecosystem structure and functioning and alterations of physical resources, nutrient quality and resident biota of whole regions because of its augmented growth rate and detrimental allelopathic properties [3,4]. In addition, consumption of this foliage by grazing animals can result in rumination, photosensitisation, anorexia, pulmonary toxicity and hepatotoxicity [5]. Within this context, this invader will lead to great declines in native biological diversity and pose significant threat to biodiversity, thus giving rise to a sequence of serious ecosystem destruction, environmental problems and socio-economic losses worldwide [6]. China is among the countries that have the greatest problems with *Ageratina adenophora* worldwide. *Ageratina adenophora* was firstly introduced into Yunnan province, China, via Myanmar in the 1940s, and then rapidly invaded into Guangxi, Sichuan, Chongqing and Guizou in southwest China and currently continuously diffuse further northward and eastward with an estimated annual speed of approximately 20 km [7,8]. It is reported that a typical *Ageratina adenophora* plant can produce up to ten thousand seeds each season, majority of which are viable and will potentially spread over long distances, enabling *Ageratina adenophora* to expand rapidly [6]. Therefore, in recent years much effort and renewed interest have been focused on the effective control and management of *Ageratina adenophora* infestation and the disposal of harvested *Ageratina adenophora*, and the costs are prohibitively ever-escalating.

This study was focused on the treatment, disposal and exploitation of this weedy plant. Utilization of *Ageratina adenophora* as biomass feedstocks for thermochemical

degradation is a promising route to control its invasion, reduce its volume and extract useful energy. Fast pyrolysis is the major anaerobic thermochemical conversion technology for targeting bio-oil production

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using reaction temperature range of 450–650 °C, high heating rate of 10^3–10^4 K/s and short residence time (< 2s) [9–11]. A considerable number of studies have been extensively undertaken about biomass fast pyrolysis, and one of fast pyrolysis processes is microwave-assisted fast pyrolysis (MAFP), which has advantages of: (1) fast and uniform internal heating of large-size particles, (2) no need for particle grinding, agitation or fluidization, (3) instantaneous response for rapid start-up and shut-down, (4) ease of control, operation and maintenance, (5) cost-effective and energy efficient and (6) cleaner products [12–16]. MAFP technique has been successfully used in producing bio-oil [17–21].

Unfortunately, it is discerned that the resultant crude bio-oil is inherently incompatible with current energy infrastructure attributing to its detrimental drawbacks of high oxygen content, low heating value, poor thermal stability, high viscosity, acidity and corrosiveness [22–24]. Therefore, crude bio-oil should be upgraded before reaching the fuel usual standard specifications, and microwave-assisted catalytic fast pyrolysis (MACFP) in the presence of catalysts is one of the most effective methods to expel oxygen content and improve bio-oil quality [25–27]. Of the dozens of catalysts that have been evaluated, it is now widely agreed upon that ZSM-5 is the best catalysts for producing hydrocarbons owing to its effective deoxygenating capacity [28–34]. However, polymerization of large reactant molecules will occur essentially on the external surface of ZSM-5 for allowing their acid catalysed transformation into bulky molecules (termed “coke”) which will remain trapped there with as an consequence a rapid catalyst deactivation [35–37]. On the other hand, adding CaO can crack the large-molecule oxygenates from pyrolysis into small-molecule compounds due to its strong cracking ability [38,39]. Lu et al. [40] conducted catalytic upgrading of biomass fast pyrolysis vapors with CaO in a tandem micropyrolyzer, and it was found that using CaO as the catalyst could significantly increase the relative content of small-molecule compounds in bio-oil. Thus, the combined use of CaO and ZSM-5 as the catalysts is a feasible way to mitigate coke formation on ZSM-5 and promote hydrocarbon production in bio-oil. When fast pyrolysis biomass vapors pass through the CaO layer, the heavy compounds in vapors will be cracked into smaller oxygenates, which will in turn be sequentially converted into hydrocarbons via ZSM-5 catalyzed transformation.

Another critical problem for hydrocarbon production through MACFP of *Ageratina adenophora* is that *Ageratina adenophora* is a hydrogen-deficient and oxygen-rich biomass feedstock, thus adversely affecting hydrocarbon production and bio-oil quality. Chen et al. [41] proposed a parameter named effective hydrogen index (EHI) to reflect the relative hydrogen content of different feedstocks. The expression of EHI is written on the assumption of debiting the compound’s hydrogen content for complete conversion of heteroatoms into H_2O, NH_3 and H_2S:

$$\mathrm{EHI} = \frac{\text{H-2O-3N-2S}}{\text{C}} \tag{1}$$

The H, O, N, S and C in Eq. (1) are the moles of hydrogen, oxygen, nitrogen, sulfur and carbon in feed, respectively. The EHI of *Ageratina adenophora* is usually less than 0.3, thus suggesting the extreme lack of hydrogen. Previous experimental results on the correlation between feedstock EHI and bio-oil production reached the following documentation: Biomass with higher EHI could produce more hydrocarbon and less coke [42]. Microwave-assisted catalytic fast co-pyrolysis (co-MACFP) of *Ageratina adenophora* with other feedstock with a higher EHI is a useful technology to improve the overall EHI of total feedstocks, fine-tune catalytic performance and inhibit coke formation [43–45].

As a vast and economically important reservoir of sedimentary organic carbon, kerogen is a mixture of complicated insoluble macromolecular organic chemical compounds that make up a portion of the organic matter in sedimentary rocks, and is the major source of carbon for hydrocarbon generation in the subsurface [46–48]. With tremendous reserves, kerogen is an important alternative to conventional petroleum resource as kerogen can yield oil when destructively distilled. The cost-effective implementation of kerogen necessitates appropriate technologies to manufacture biofuels, and pyrolysis is more amenable to extract hydrocarbon fuel from kerogen [49,50]. Additionally, the EHI of kerogen is about 1–2, indicating that it is a good hydrogen donor for co-feeding with *Ageratina adenophora*. Accordingly, utilization of kerogen in co-pyrolysis is a potential solution to improve bio-oil quality and minimize coke formation. Nonetheless, to the best of our knowledge, catalytic co-pyrolysis technique of *Ageratina adenophora* and kerogen has not been studied.

Herein, this study aims to demonstrate the ideal exploitation of *Ageratina adenophora* as nontraditional carbon-based feedstock for fuel recapture. The primary objective of this work is to study co-MACFP of *Ageratina adenophora* and kerogen mixtures in a microwave heating reactor with CaO and ZSM-5 as the catalyst to see if the hydrocarbon production can be facilitated or coke formation can be diminished. The effects of reaction temperature and CaO to ZSM-5 ratio on MACFP of *Ageratina adenophora* to kerogen are studied to determine a suitable operation condition for co-MACFP of these feed mixtures. We compare the relative content of hydrocarbons in bio-oil and yield of coke from individual MACFP of *Ageratina adenophora* and kerogen and co-MACFP of their mixtures to elucidate the potential benefits of co-feeding. This paper thus provides essential insight into how the hydrocarbon production can be promoted or coke formation can be restrained by coprocessing *Ageratina adenophora* with kerogen.

2. Experimental

2.1. Materials

2.1.1. Feeds

Ageratina adenophora is purchased from a forestry center in Lancang County of Yunnan Province, South China. Likewise, kerogen is purchased from Kunming University of Science and Technology in the city of Kunming in Yunnan Province, South China. Prior to reactions, both *Ageratina adenophora* and kerogen are dried at 105 °C for 24 h, and then smashed with a high-speed rotary cutting mill and sieved through a 40-mesh sieve. The component analysis of the dried *Ageratina adenophora* is 28.44 wt.% cellulose, 23.23 wt.% hemicellulose, and 16.17 wt.% lignin. During pyrolysis, thermal decomposition of cellulose and hemicellulose will lead to the generation of anhydrosugars. Then the anhydrosugars will undergo rearrangement or dehydration reactions to form oxygenates. Meanwhile, thermal decomposition of lignin will lead to the generation of phenols. When these oxygenates pass through the ZSM-5 layer, some of them will be converted into hydrocarbons (especially aromatics). Additionally, the ultimate analysis of feedstock is determined using an elemental analyzer (CE-400, Exerter Analytical Inc., USA) according to the operation manual (combustion furnace emperature: 950 °C, reduction furnace temperature: 770 °C). For proximate analysis, moisture content is determined by mass difference after biomass sample is dired at 105 °C for 10 h in a drying oven; volatiles are determined by mass difference after biomass sample is thermally treated at 900 °C for 7 min under inert atmosphere; and the ash content is calculated by mass difference after biomass sample is combusted at 815 °C. The proximate analysis of the dried *Ageratina adenophora* is 9.94 wt.% moisture, 81.16 wt.% volatile, 3.01 wt.% ash, and 5.89 wt.% fixed carbon (by difference). The elemental composition of the dried *Ageratina adenophora* is 44.16 wt.% carbon, 5.76 wt.% hydrogen, 44.19 wt.% oxygen, and 0.74 wt.% nitrogen. On the dry basis the approximate molecular formula of *Ageratina adenophora* is therefore $C_{3.68}H_{5.76}O_{2.76}N_{0.05}$, and the EHI of *Ageratina adenophora* is 0.02. The elemental composition of the dried kerogen is 67.63 wt.% carbon, 8.87 wt.% hydrogen, 10.31 wt.% oxygen, and 0.96 wt.% nitrogen. On the dry basis the approximate molecular formula of kerogen is therefore $C_{5.64}H_{8.87}O_{0.64}N_{0.07}$, and the EHI of kerogen is 1.31.