



# Study on catalytic co-pyrolysis of physical mixture/staged pyrolysis characteristics of lignite and straw over an catalytic beds of char and its mechanism



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## ABSTRACT

Although the study of co-pyrolysis of coal and biomass have dominated the primary chemicals production in the field of renewable energy utilization, it is still challenging for tar to become lighter. Here we design a set of experimental programs, including the individual pyrolysis, staged catalytic pyrolysis and the co-pyrolysis of physical mixture to investigate the effects of feedstock arrangement on pyrolysis product characteristics. We demonstrated that the experimental results of co-pyrolysis of physical mixture indicate some synergetic effects on pyrolysis products rather than the superposition of individual pyrolysis process of lignite and straw, thus the subsequent tar composition and char structure were characterized. Based on the existing catalytic cracking mechanism, we obtained the staged catalytic pyrolysis have a more pronounced catalytic cracking effect on heavy components compared with the co-pyrolysis of physical mixture, which enables the formation of light oil, naphthalene oil, tar with the lower oxygen content and higher benzene. The Raman spectra of char in catalytic bed exhibits the total peak area of char and the amount of large aromatic ring formed by polymerization increased with the increase of pyrolysis temperature. Simultaneously, the role of catalytic cracking of straw char was stronger than that of lignite char remarkably has been confirmed from the point of view of the chemical structure of char.

## 1. Introduction

Lignite utilizations are limited due to the disadvantages of lignites such as high moisture content, high ash yield, and low calorific value [1,2]. Direct combustion and other conventional utilization processes of lignites will emit a huge amount of CO<sub>2</sub>, leading to catastrophic global warming. Accordingly, mild and eco-friendly utilization technologies should be paid attention to overcome the disadvantages [3,4]. The co-pyrolysis technology of lignite and biomass can be used to prepare liquid fuels and chemicals by one-step conversion. It is considered as the most promising way to realize the large-scale and effective utilization of lignite and renewable resources, and realize the reduction and energy utilization of straw and other wastes, and substitute biomass for fossil fuels, and reduce the greenhouse gases such as CO<sub>2</sub>, CH<sub>4</sub> and SO<sub>2</sub> emissions [5–7]. It is necessary to highlight that the co-pyrolysis of lignite and biomass based on the possible synergy effect has been considered as promising alternatives, because it not only can change the structure of co-pyrolysis liquid products, but also can improve the

quality of products. However, there is always a disagreement concerning if the reactions must be included in the synergy effect.

Although co-pyrolysis is a mild thermal conversion process, it is an important means to obtain low carbon fuels and high value-added chemicals directly from feedstock. However, common pyrolysis is usually carried out by physical blending of experimental samples at a certain proportion [8]. The condensation products of primary volatile from individual pyrolysis of lignite and biomass are mainly composed of aromatic compounds (benzene series, phenols and nitrogen compounds) and macromolecular oxygenated compounds, which have low interaction activity, high content of asphaltene [9] and high viscosity in tar [10]. While the low tar yield [11–13] are the main problems in the development of this technology. The fundamental reason is that the pyrolysis characteristics of different experimental samples are quite different. Moreover, further studies of synergistic effect in the co-pyrolysis and the development of related processes were carried out using different rank coal similar to that described elsewhere by Wu et al. [14] and Meng et al. [15]. For example, pyrolysis experiments based on

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thermal analysis balance and different reactors show that the synergistic effect in pyrolysis process is mainly reflected in the pyrolysis products, but the difference between tar and volatile is not enough to prove the synergistic effect between them. Some studies have shown that alkali and alkaline earth metals (AAEMs) has catalytic effect on coal pyrolysis during the co-pyrolysis process [16–18]. It is believed that the more lighter co-pyrolysis tar in the process of coal pyrolysis can be achieved by effectively utilizing the active substances contain hydrogen free radicals (H<sub>•</sub>) released from biomass pyrolysis. To achieve a better understanding of how the experimental parameters affect heavy components, it seems that the previous research mainly focus on the co-pyrolysis of coal and biomass under the same reaction conditions (such as the same residence time, pyrolysis temperature and heating rate) [19,20]. Nevertheless, the whole reaction process parameters cannot be controlled effectively, and the research methods are also generally limited.

In this regard, the catalytic upgrading of coal tar and the catalytic co-pyrolysis of lignite and biomass (including catalytic cracking of co-pyrolysis tar and direct catalytic co-pyrolysis of physical mixture of experimental samples and catalysts) have been the research focus in the field of clean energy and chemical industry. For example, Wang et al. [21] have investigated tar reforming using char as catalyst during pyrolysis and gasification of Shengli brown coal, which shows that the activated char as catalyst has a much better catalytic performance for tar reduction than the inactivated char. The catalytic reforming reactions could also cause the increase in the proportion of large aromatic rings in tars, whereas the presence of steam in the reaction zone could see the decrease of large aromatic rings in tars. Moreover, the authors have identified the correlation among the some defects on the surface of char with certain aromaticity and active sites of tar cracking reaction [21]. In particular, they have observed that some active components in the char. For example, AAEMs can make the free radical fragments in tar react with each other to form precipitated carbon, which can effectively promote the cracking reaction of tar, and then realize the upgrading of tar [21]. In addition, it should be pointed out that biomass and coal have different chemical and physical properties, i.e., ash composition, volatile matter, H/C, and O/C molar ratio. These differences in the properties lead to different reactivity and thermal characteristic during co-pyrolysis. It is believed that high thermo chemical reactivity and high content of volatiles in biomass will facilitate the conversion and the upgrading of the fuel, biomass with high H/C ratio could act as hydrogen donors in co-pyrolysis of biomass/coal blends [22].

Considering the above analysis, the pyrolysis can be considered as a single and independent process to produce liquid fuels and chemicals [23–25], but the production of fuels and fine chemicals from coal is limited due to the low H/C ratio. Supplying the hydrogen by addition of biomass can increase the thermal conversion and product yields. During the co-pyrolysis of coal and biomass, a synergy effect can be expected to produce more volatiles. Synergetic effect in co-processing of coal and biomass has been reported in the literature [26–28]. Although considerable progress has been made, particularly in the last ten years. However, some expected and intriguing findings are still matter of debate. Some authors pointed out that AAEMs gives rise to stronger active sites, whose presence favors the cracking reaction [29,30]. Other authors proposed that the tar upgrading reaction occurred in gaseous phase, which was mainly caused by the secondary reactions. Alternatively, it has been suggested that no synergetic effect was observed in gas, liquid and solid yields [31].

Moreover, the previous investigations were concerned on the pyrolysis conditions required to obtain a maximum oil yield as well as pyrolysis kinetics. Additionally, theoretical achievements for the importance of AAEMs has catalytic cracking effect on tar, and the active sites catalyze decomposition of heavy fractions by adsorption and dissociation has been also presented [32,33]. However, the published literatures mostly focus on the effects of experimental conditions,

feedstock properties and reaction kinetics parameters on the structure, distribution and properties of co-pyrolysis products. There are few data that provide insights into the impact of strengthening synergistic effect on fundamental chemical reaction of second thermal cracking. In particular, our knowledge regarding intrinsic reactivity behavior, which is the fundamental component of volatile compounds with higher activity and smaller molecular weight were obtained from second thermal cracking of primary volatiles from individual pyrolysis coal and biomass, is limited and incomplete. It should be pointed out that the in-depth exploration and analysis of the synergistic mechanism of the whole catalytic cracking process is also scarce. In order to qualitatively trace product distribution from pyrolysis of coal with different structural models. He et al. [34] researched the correlation of pyrolysis products and the breakage of different bonds by TG–GC–MS. Moreover, many researches indicated that the release of organic compounds is affected by the coal structure [35,36]. However, not enough attention has been dedicated in previous studies to the influences of differences in structure and composition between lignite char and straw char on pyrolysis products properties, not to mention catalytic bed with layered placement. Systematic studies specifically centered on the behaviors of co-pyrolysis of physical mixture of coal and straw, and staged catalytic pyrolysis of coal and straw in this paper.

Therefore, with the aim to solve the problems mentioned above, the significant innovation in this work are to:

- (1) Investigate the pyrolysis product's characteristics from co-pyrolysis and primary catalytic pyrolysis were carried out by the three layer fixed bed reactor.
- (2) Study effects of catalytic co-pyrolysis of physical mixture and staged catalytic pyrolysis of coal and straw by layered placement on gas components, tar fractions and light oil yield.
- (3) A range of techniques was applied to analyze the change of the content of intrinsic mineral in catalytic char bed, chemical structure of catalytic char and the oxygen content in tar during co-pyrolysis and primary catalytic pyrolysis, which significantly influences the reaction activity in the further chemical conversion process.

In this work, a typical Chinese lignite from Inner Mongolia XilinGol were chosen as the experimental coal sample and the corn stalks (straw) were collected in the countryside of Miyun, Beijing. This study was designed to compare the different changes in the physicochemical structure characteristics of the pyrolysis product, such as the tar composition, intrinsic mineral content in char due to the different layered placement. Additionally, this work also can expand the possibility of upgraded coal tar with an efficient and selective pyrolysis method to improve light oil yield by using staged catalytic pyrolysis. On this basis, the outcome of this study can provide new knowledge and necessary basic data for better understanding the conversion path and mechanism analysis of light oil produced from the individual catalytic pyrolysis, co-pyrolysis of physical mixture and staged catalytic pyrolysis of heavy tar.

## 2. Experiment

### 2.1. Sample

In this experiment, a typical Chinese lignite from Inner Mongolia XilinGol were chosen as the experimental coal sample and the corn stalks were picked up in Beijing Miyun countryside. Firstly, the coal samples and straw will be crushed to below 1 mm by high-speed crusher and sieved by 80 mesh standard screening. Then samples were placed and labeled in sealed containers and then stored in a refrigerator after drying for 12 h at 105 °C under vacuum condition. At length, the results of experimental samples were obtained and its proximate and ultimate analyses according to Chinese National Standards GBT212-2008 were given in Table 1. Raw ash samples for the investigation of minerals transformation were prepared at 815 °C based on GB/T 1574-2001. The

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