Products distribution during in situ and ex situ catalytic fast pyrolysis of Chinese herb residues

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Abstract
Catalytic fast pyrolysis (CFP) for biomass treatment is a research hotspot but there is little information about the difference between in situ and ex situ methods. In present work, the Ni–Fe/CaO–Al2O3 catalysts with different Ni/Fe ratios have been synthesized by coprecipitation method, and the product distribution about the Chinese herb residue (CHR) catalytic fast pyrolysis by in situ and ex situ methods in a quartz tube reactor system has been investigated. The results show that the CFP pyrolysis would upgrade the quality of bio-oil but decrease the yields, no matter in situ or ex situ CFP process. During the in situ CFP process, heteroatoms may be absorbed by the catalyst support and cannot be transferred to the bio-oil, but the results of ex situ CFP are the opposite. In addition, the ex situ CFP reaction significantly increases the content of aromatic hydrocarbons. As to the gas products’ distribution, the effect of Fe in catalysts to promote CH4 formation is reflected in in situ CFP process, while the promotion effect of H2 generation for Ni added in catalyst is mainly reflected in ex situ CFP process. However, due to the high reaction temperature (800 °C), the adsorption of CO2 by CaO support is not particularly significant. The possible mechanism of CHR in CFP process has also been summarized for understanding the process of in situ and ex situ CFP, and this study may provide a choice or reference for CHR treatment.

Keywords Chinese herb residue · Catalytic fast pyrolysis · In situ · Ex situ · Product distribution

Introduction
In recent years, the energy utilization of waste biomass had received great attention in order to alleviate the future fossil fuel overuse, global warming, and environmental pollution (Hu & Gholizadeh 2019). According to a recent report by Xing et al., the biomass had a significant potential for bioenergy utilization in China (Xing et al. 2021). But the shortcomings of biomass were also obvious, such as high moisture and volatile matter content, low bulk and energy density, and high ash content (Chen et al. 2018), which restrain the direct utilization, storage, and transportation of raw biomass. Therefore, it was important for biomass to convert bio-oil, biochar, and inflammable gas by thermochemical ways (Liao et al. 2020). The catalytic fast pyrolysis (CFP) was a preferred way to convert biomass into bio-oil with high heating values, which had been evaluated comprehensively by Xu et al. (Chen et al. 2019) and it was beneficial to obtain high quality and yield bio-oil. Cai et al. (2021) summarized the raw materials and reactors for biomass fast pyrolysis; they thought that the key for energy conversion of biomass was to overcome the seasonal supply and low catalytic pyrolysis efficiency. Thus, a stable supply of biomass feedstock was conducive to the continuity of catalytic fast pyrolysis as well. Chinese herb residues (CHR) were a solid biomass waste of which the production is more than 15 million tons every year; it was suitable for energy utilization and overcoming feedstock supply (Zhao et al. 2019). However, catalysts and catalysis methods had also a significant impact on the distribution and quality of the products of CFP. A review summarized by Kim et al. (2019) demonstrated that bifunctional catalysts were more suitable for the biomass pyrolysis in terms of remission catalyst deactivation.
and coke deposition. More recently, Jin et al. (2022) found catalytic pyrolysis significantly decreased the oxygen ratio of bio-oil and increased the higher heating value, and basic catalysts were expected to neutralize the acid in bio-oil. Certainly, for pyrolysis catalysts, catalytic centers and the structures of the support were all important about their performance. The Ni–Fe-based catalyst had been widely reported due to their excellent mutual promotion catalytic performance in tar cracking and gas upgrading (He et al. 2020; Liang et al. 2020; Wang et al. 2011). Yue et al. (2021) synthesized a biochar-supported Ni catalyst to obtain methane-rich gas and found it conducive to the tar converted into gas production. Lu et al. (2021) had investigated the deactivation of Fe catalyst and they found it to have been wrapped and covered by coke during the catalytic pyrolysis, which was the main reason for restraining the activity of Fe catalyst. Wang et al. (2020) found Fe–Ni bimetallic catalyst had a stable catalytic reaction performance, and it combined the advantages of two metal elements during the catalytic pyrolysis. Lin et al. (2021) had synthesized a char-supported Ni–Fe catalyst with the hierarchical structure; they found it had high reaction activity for cracking tar, and the special structure would enhance the ability of deactivation and sintering of the catalyst. Li et al. (2022) investigated the deactivation mechanism of Ni–Fe catalyst and they found the activity of catalyst decreased due to the cumulative biomass/catalyst ratio, but it was able to maintain the aromatic selectively of bio-oil, so it was necessary to control the ratio of biomass to catalysts. In addition, the Ni–Fe catalyst had also application in another thermochemical conversion field, especially in fast pyrolysis of waste plastics (Cai et al. 2020; Chen et al. 2020; Yao et al. 2021). As to supports, Al₂O₃ was a suitable carrier for pyrolysis catalysts because of its physical and chemical stability (Arregi et al. 2018). According to the report by Fernandez et al. (2021), Al₂O₃ supports had severe catalytic acidity to increase the bio-oil cracking, which was conducive to the gas formation and enhance the CO content. Furthermore, in order to reduce the CO₂ compounds in gas, the CaO had also been used as one of the pyrolysis catalyst supports. Calcium oxide was a low-cost, highly effective, and non-toxic support material which was reviewed by Li et al. (2021), regardless if in pyrolysis or in gasification of biomass. Nam et al. (2020) found that the presence of CaO in biomass gasification process would promote the water–gas shift reaction and enhance the H₂ concentration of products due to the CO₂ absorbed, and this phenomenon had also been reported by Liu et al. (2019) about chemical looping gasification of biomass. Besides in situ CO₂ capture, Hu et al. (2020) demonstrated that CaO plays as the catalyst and forms a new phase by reacting with Fe₂O₃, which was also conducive to the yield of H₂. Gupta et al. (2021) investigated the multi-route conversion of CaO catalyst and demonstrated the effective and stability structure of CaO during the catalytic fast pyrolysis of biomass to upgrade the pyrolytic products and obtained value-added chemical and fuel precursors. So the dual-support catalysts of Al₂O₃ and CaO with Ni–Fe were worth exploring.

Furthermore, the in situ and ex situ catalytic methods were crucial for catalytic pyrolysis products. However, very few had simultaneously compared the difference of in situ and ex situ fast catalytic pyrolysis. The motivation of the present work was to investigate the production distribution of in situ and ex situ catalytic fast pyrolysis of CHR with the Ni–Fe loaded Al₂O₃/CaO, which may provide a new way for the energy utilization of CHR.

Materials and methods

Materials

Chinese herb residue taken from Jiuzhitang Co., Ltd. (Changsha, China), and its ultimate and proximate analysis are reported by our previous work (Huang et al. 2021). The ultimate and proximate analysis of CHR is shown in Table 1. Before performing the pyrolysis experiment, the raw CHR had been dehydrated and milled through a 100-mesh sieve. Some analytical reagents, including Ni(NO₃)₂·6H₂O, Fe(NO₃)₃·9H₂O, Ca(NO₃)₂·4H₂O, Al(NO₃)₃·9H₂O, NaOH, and Na₂CO₃, were purchased from the Chemical Reagent Co., Ltd., China Pharmaceutical Group, which were used to synthesize catalysts.

Catalyst synthesis and characterization

The Ni–Fe/Al₂O₃ catalysts with the different ratio of Ni/Fe were synthesized by coprecipitation method. The mass ratio of reagents was performed by the ratio of the total of Ni–Fe and the total of CaO–Al₂O₃ of 1:4. Particularly, the molar ratio of Ni and Fe was kept in 0:1, 1:3, 1:1, 3:1, and 1:0, and these catalysts were denoted as NiFe-1, NiFe-2, NiFe-3, NiFe-4, and NiFe-5, respectively. During the coprecipitation process, reagents were mixed according to mass ratio and dissolved in deionized water. This aqueous solution was heated to 70 °C and was constantly stirred. Later, precipitate solution was added which made up NaOH and Na₂CO₃ of 1:1 and the remaining was stirred for 60 min. After 10 h of aging, the crystals precipitated were separated from the solution and dried at 105 °C for 12 h and then calcined at 800 °C for 4 h in air atmosphere. Finally, the solid samples were reduced in 10 mL/min H₂ and 90 mL/N₂ atmosphere to obtain catalyst. In order to investigate the surface microstructure of the catalyst, the surface crystal structure of the catalyst was scanned in the range of 10° to 80° with XRD-6000 diffractometer (Shimadzu Corporation, Japan), and the specific surface area and total pore volume
were measured with KuBO-X1000 machine (Beijing Builder Electronic, China).

**Pyrolysis conditions and product analysis**

The in situ and ex situ catalytic fast pyrolysis experiments are performed in a quartz tube reactor system shown in Fig. 1, and the size of the device was the same as that in our previous report (Huang et al. 2021). During the in situ CFP process, catalyst and CHR were mixed in 1:1 ratio in quartz boat and the total amount is 10 g, and were then put into the tube of furnace. In a nitrogen flow of 100 mL/min, samples were heated from room temperature to 800 °C with 10 °C/min. The ex situ CFP process was the same as in situ CFP process; only the CHR and catalyst were placed in quartz boat and catalytic device, respectively. After the tube furnace temperature was stabilized at 800 °C, the quartz boat containing the sample was pushed into the constant temperature zone of the furnace by putter, and kept at constant temperature for 1 h. The products of bio-oil and gas were collected by condensation unit and gas collecting bag, respectively. Obviously, the char remains in the quartz boat. The mass balance calculation method of pyrolysis products, the extraction and analyzed method of bio-oil, and the gas analysis were consistent with our previous report (Huang et al. 2021).

**Results and discussion**

**The characterization of catalysts**

According to the XRD spectra in Fig. 2, the crystal structure of Al2O3, Fe2O3, CaO, Ca(OH)2, and NiO was detected in catalyst precursors. After hydrogen reduction, a new phase of metal Ni appeared in catalysts. A small amount of moisture was adsorbed and reacted by CaO support in the catalysts, which might be the only reason for detection of Ca(OH)2. The diffraction peak intensity of NiO/Ni and Fe2O3 was consistent with the relative load of Ni and Fe element. The Fe2O3 in catalysts had not been reduced because Fe atoms had stronger O affinity in catalyst which made it difficult to be reduced to Fe metal. In addition, the BET surface area and pore volume of catalysts are shown in Table 2, and it was clear that bimetal load samples like NiFe-3 and NiFe-4 have a smaller specific surface area and pore volume than single load like NiFe-1 and NiFe-5, but NiFe-2 has the largest specific surface area and pore volume.

**The product distribution of in situ and ex situ pyrolysis**

The distribution of gas, bio-oil, and char of in situ and ex situ CFP of CHR is shown in Fig. 3a and b, respectively.
Generally, the char and bio-oil yields in in situ CFP pyrolysis are lower than those in ex situ, while the gas yields are relatively higher. This phenomenon is consistent with the different reaction mechanism of in situ and ex situ CFP. Catalysts interact directly with the solid biomass when they blend with CHR, which would favor the thermal decomposition of the feedstock and result in less residual char. However, in ex situ CFP process, catalysts are only for catalytic reforming of the volatiles after biomass pyrolysis.

![Quartz tube reactor system](Fig. 1)

![XRD spectra of Ni–Fe/CaO–Al2O3 catalyst with different loading amount of Ni and Fe: a before reduction; b after reduction](Fig. 2)

### Table 2 Textural properties of the catalysts

| Catalysts | BET surface area (m²/g) | Pore volume (cm³/g) |
|-----------|-------------------------|---------------------|
| NiFe-1    | 7.12                    | 0.07                |
| NiFe-2    | 8.96                    | 0.09                |
| NiFe-3    | 5.35                    | 0.05                |
| NiFe-4    | 4.84                    | 0.05                |
| NiFe-5    | 8.42                    | 0.07                |
decomposition, and this process will result in the reforma-
tion of volatiles and the formation of bio-oil compounds,
so ex situ CFP enhances the yield of bio-oil. As to the dif-
ferent ratios of Ni and Fe in catalysts, more Fe contents in
catalysts seem to enable more char and bio-oil, while the
gas generation should be promoted with the increase of
Ni content in catalysts. This is due to the fact that Ni con-
tributes to the secondary cracking of the bio-oil, which is
more pronounced in ex situ CFP process (Lu et al. 2020).
Nevertheless, the effect of different catalysts on prod-
uct distribution is not very obvious, especilly in NiFe-2,
NiFe-3, or NiFe-4, which may be due to some synergy
between Ni, Fe, and the catalyst support. Compared to the
CK group, both in situ and ex situ CFP seem to reduce the
yield of bio-oil and increase the yield of gas, which may be
due to the fact that the catalyst promotes the fragmentation
of macromolecular structures in the feedstock and thermal
decomposition volatile matter.

**Gas composition of in situ and ex situ CFP**

As can be seen in Fig. 4, there are relatively large differ-
ces between the gas composition of in situ and ex situ
CFP process, but the regular patterns of Fe and Ni effects
on gas composition are unified in two pyrolysis methods. Fe
added in catalysts would promote the CH₄ formation and Ni
added would enhance the H₂ yield (Huang et al. 2021; Qu
et al. 2021). The catalytic effect of H₂ yield in in situ CFP
is weaker than that in ex situ because the former catalysts
act directly on biomass feedstock while the latter catalysts
act on volatile matter, and the catalytic pyrolysis targeting
volatiles is more likely to promote the cleavage of C–H to
form H₂ (Cao et al. 2021). CO₂ contents were less than those
in our previous studies (Huang et al. 2021) that was because
a part of the CO₂ has been absorbed by CaO in catalyst sup-
port. And the CO content is increasing gradually with the
Ni increasing in in situ CFP process, but it is not obvious
the regularity in ex situ CFP pyrolysis; this may be due to
the fact that Ni in the catalyst promotes the decarbonyla-
tion reaction mainly in the reaction with biomass feedstocks
rather than volatile matter (Van de Velden et al. 2010). In
addition, the deposition coke in the surface of catalyst sup-
ports may react with CO₂ and convert it to CO at high tem-
perature, which may be another resaon that the CO content
is generally higher than CO₂. This phenomenon is consistent
with the results of Gao et al. (2021) that the presence of CaO
would absorb CO₂ and increase the H₂ content in gas prod-
ucts. In the CK group without catalyst, the content of CH₄
seems to be higher than that in the CFP experimental group.
But as the matter of fact, during the pyrolysis reaction, there
are many conversion paths between CH₄ and H₂, and CO
and other gases, and the process is quite complicated (Yun
et al. 2020), so it is difficult to follow or discuss in this part.

**Effect of catalytic methods on bio-oil compounds**

Bio-oil is the most important product for biomass CFP. It
is also an important energy carrier and precursor of chemi-
cal products. Besides yield, the composition of bio-oil also
plays a crucial role in its utilization value. The basic clas-
sification of in situ and ex situ catalyzed bio-oils are shown
in Fig. 5a and b, respectively. Whether it is in situ or ex situ
CFP process, the main components of bio-oil are aromatics
which originate from the decomposition of aromatics

structures in lignin or the Diels–Alder reaction by olefins (Safdari et al. 2019). In composition, the content of heterocyclics and aliphatics is much lower, which was consistent with our previous studies because of the physical and chemical properties of CHR (Auersvald et al. 2020; Huang et al. 2022). The results also show that the catalytic method has little effect on the distribution of the three types of components in bio-oil. In contrast, the increase of Ni in the catalyst during the ex situ CFP process is more conducive to the selective generation of aromatics.

The detail functional compound contents of bio-oil are shown in Fig. 6. Apparently, aromatic hydrocarbons (Ar–H) is the most content in bio-oil, and the secondly is phenol. This phenomenon also demonstrated that the aromatization is a major reaction in the CFP process to form bio-oil (Liu et al. 2021). However, there are quite different effects about the Ar–H content in bio-oil between in situ and ex situ CFP process. In in situ CFP, higher Ni/Fe ratio in the catalyst tends to generate more aromatics, and the highest is in NiFe-4, but it is not conducive to the formation of phenols. In Fig. 6a, the content of phenols decreases gradually with the increases of Ni/Fe ratio. This may be due to the fact that in the process of in situ CFP process, the total amount of aromatic substances generated by the interaction of raw materials and catalysts is constant, and they obey the distribution principle in the process of forming aromatic hydrocarbons.

![Fig. 4 Gas composition of in situ (a) and ex situ (b) catalytic fast pyrolysis](image1)

![Fig. 5 Heterocyclics, aliphatics, and aromatics contents of pyrolytic bio-oil: a in situ CFP; b ex situ CFP](image2)
and phenols. Moreover, after the in situ catalytic reaction is completed, the decomposed volatiles cannot form new aromatic hydrocarbons because they no longer have the effect of catalyst, so this phenomenon appears in the in situ CFP process.

Compared with in situ CFP, there was less phenol appearance but more Ar–H content in ex situ CFP, which was also determined by two different methods of catalysis. In addition, heteroatoms in in situ CFP bio-oil are lower than those in ex situ CFP; this may be due to CaO and Al₂O₃ as catalyst supports in in situ CFP react with heterostoms, leaving them in the solid product, and resulting in relatively low content of heteroatoms in bio-oil. Meanwhile, in ex situ experiments, it is clearly showed that heteroatoms increase gradually with the increase of Ni/Fe ratios. Firstly, in ex situ CFP process, there are no catalyst and catalytic carrier during the thermal decomposition process of CHR, which results that the heteroatoms in CHR easily enter the second reaction stage with the release of volatile matter. Later, this volatile matter reacts on the catalyst surface to form bio-oil, and the heteroatoms in the volatile matter are transferred to the bio-oil. Secondly, as the Ni/Fe ratios increase, more hydrogen in the volatiles matter is converted into hydrogen by the nickel in the catalyst, which provides more sites for the binding of heteroatoms to carbon atoms, and it may also be an important reason for the high content of heteroatoms in bio-oil obtained by ex situ CFP. As to another compound in bio-oil, such as alcohol, acid, and ester, they are present in extremely low amounts and with little regularity in their distribution, especially in ex situ experiments. In general, single iron-containing catalyst (NiFe-1) is beneficial for the formation of more functional species in bio-oil, either in situ or ex situ CFP. Furthermore, in situ CFP tended to form more alcohol and ketone (Luo et al. 2021), but ex situ CFP tended to form more ethers.

The relative content of different carbon numbers in bio-oil compounds is shown in Table 3. In general, the main composition of CFP bio-oil is light compounds (C₄–C₁₁), and in situ CFP process, more Fe added in catalyst is conducive to much light compounds. This phenomenon indicates that

| Table 3 The carbon numbers distribution of in situ and ex situ CFP bio-oil |
|---------------------------------------------------------------|
| **Catalysts** | **Relative content (area%)** |  | **Ex situ** |  |  |
|               | **C₄-C₁₁** | **C₁₂-C₂₀** | **C₂₀+** | **C₄-C₁₁** | **C₁₂-C₂₀** | **C₂₀+** |
| NiFe-1        | 90.93      | 8.40        | 0.67     | 56.23       | 43.20        | 0.57     |
| NiFe-2        | 89.60      | 10.40       | 0        | 70.40       | 29.15        | 0.45     |
| NiFe-3        | 93.40      | 6.60        | 0        | 66.47       | 33.53        | 0        |
| NiFe-4        | 66.30      | 33.70       | 0        | 62.08       | 37.92        | 0        |
| NiFe-5        | 66.40      | 33.60       | 0        | 57.47       | 42.53        | 0        |
| CK            | 73.20      | 25.70       | 1.10     | 73.20       | 25.70        | 1.10     |
heavy oil (C20+) compounds may be more easily decomposed into aliphatic compounds under the action of catalysts with high Fe content and low Ni content. During the in situ catalytic CFP process with high Ni added, the content of diesel compounds (C12–C20) is also increased to a certain extent. The increase in the content of diesel compounds (C12–C20) can be clearly observed from Table 3, because of the significant secondary catalytic effect on volatiles in the ex situ CFP process.

**Mechanism of CHR thermal decomposition during the in situ and ex situ CFP process**

Based on the distribution of gas and bio-oil, the possible mechanism of CHR in CFP process is shown in Fig. 7. During the in situ CFP process (Fig. 7a), the catalyst is in direct contact with the CHR, and the catalyst support will also react directly with CHR (Zhou et al. 2021). This process makes a small amount of heteroatoms in the CHR absorbed and bound by alumina oxide or calcium oxide in the catalyst, which reduces the probability of heteroatoms in the CHR entering the volatiles. Meanwhile, some CO₂ might be reacted by CaO in the catalyst support to form CaCO₃ when it is produced, which results in a lower CO₂ content in pyrolytic gas of in situ CFP than ex situ CFP. In addition, compared with ex situ CFP, the addition of Ni in the in situ catalyzed reaction catalyst does not seem to have a particularly significant effect on the H₂ yield, which may be due to the fact that Ni contributes to the generation of H₂ mainly in the secondary reaction of volatiles (Shen et al. 2014), while the contact time between the catalyst and the volatiles is very short and uneven during the in situ CFP process. And the direct contact between the catalyst and the CHR feedstock that affects the generation of H₂ promotion is very limited.

However, the ex situ CFP process is shown in Fig. 7b; heteroatoms in CHR are released from feedstock after thermal decomposition and transferred to volatiles. The heteroatoms have been bound in the volatiles by covalent bonds, and the catalyst support does not seem to adsorb the heteroatoms in the volatiles during the ex situ CFP process, which leads to the majority of the heteroatoms generated during the ex situ CFP process entering into bio-oil. Nevertheless, the CFP process may be more conducive in the generation of aromatics in bio-oil.

**Conclusion**

The difference of in situ and ex situ CFP process about product distribution has been investigated in the present work, and the possible mechanism of CFP process has also been surmised. The results show that in situ and ex

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**Fig. 7** Mechanism of CFP process of CHR: a in situ; b ex situ
situ CFP of CHR have little effect on the types of pyrolytic products but have different effects on their content and changing trends. The quality of bio-oil is improved for in situ CFP pyrolysis, while relatively more bio-oil can be obtained for ex situ CFP reaction. For the role of catalyst, the promotion effect of Fe on the generation of CH₄ is more significant in situ CFP, while the promotion effect of Ni on the generation of H₂ is mainly reflected in ex situ CFP. The content of heteroatoms in the bio-oil of ex situ CFP is significantly lower than that of ex situ CFP. Compared with the CK group, the adsorption of CO₂ on the CaO supports is mainly reflected in the in situ CFP process, but the amount of adsorption is small. Overall, both in situ and ex situ CFP can achieve the upgrading of the pyrolytic products of CHR, but the product distribution characteristics are also quite different for the different mechanisms of reactions. The research in the present work may provide a reference for the catalytic fast pyrolysis treatment and utilization of Chinese herb residues or other waste biomass.

Author contribution Bo Li: conceptualization, writing—original draft; Zehao Qian: investigation, data curation; Jie Qin: visualization; Qian He: data curation; Shengxiong huang: data curation; Hang Dong: visualization; Nan Zhou: supervision; Mao Xia: writing—review and editing; Zhi Zhou: visualization.

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Data availability The data that support the finding of this study are available from the corresponding author upon the reasonable request.

Declarations

Ethics approval The authors declare that their study is compliant with ethical standards.

Consent for participate All the authors listed consent to participate.

Consent for publication We confirm that this manuscript has not been published elsewhere and is not under consideration by another journal. All authors have approved the final manuscript and agreed with its submission to Environmental Science and Pollution Research.

Competing interest The authors declare no competing interests.

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