

Fast Pyrolysis of Napier Grass Catalyzed by Encapsulated Cu([H₄]salen)

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ABSTRACT: *Napier grass can serve as a feedstock for bio-oil production, and the aim of this work comparatively evaluated the effect of catalysis by Cu([H₄]salen) on pyrolysis of Napier grass relevant to bio-oil generation. The bio-oil, char, and gas produced during the pyrolysis of Napier grass were identified and quantified. The chemical composition of bio-oil was correlated with the catalysis. Bio-oil quality was analyzed by characterization, with a high content of phenolics, low content of oxygen and a high heating value on the catalytic effect. The results obtained in this work suggested that a significant improvement has been proven with respect to bio-oil quality compared to what has been reported in the literature.*

KEYWORDS: *Cu([H₄]salen); Pyrolysis; Catalysis; Bio-oil; Compositional analysis; Napier grass.*

INTRODUCTION

Fossil fuel is increasingly exhausted with the rapid development of modern industry, besides, energy and environmental crisis force people not only to look for new alternative energy sources, but also optimize the utilization of the existing resources [1]. In recent years, the use of perennial feedstocks has attracted more and more attention [2, 3], of which Napier grass can be converted into bio-oil by pyrolysis [4, 5]. Napier grass is endemic to Africa and distributed all over the world. It is a tall perennial weed. Napier grass is easily exposed to light, water and nutrients. Napier grass has been using in farming feed [6]. It has other applications in industry as well, such as new energy [7-9].

At present, bio-oil still has some disadvantages, such as poor stability, high viscosity, strong corrosivity as well as higher oxygen content, it is hence needed to study new catalytic process in biomass pyrolysis [10]. The catalysts used in biomass pyrolysis including alkali metal, alkaline earth metal [11], metal oxides [12], zeolites [13] and mesoporous materials [14].

As an alternative approach to enzyme, metal salen complexes are considered as a promising catalyst in the field of green chemistry due to their biomimetic performances [15]. Ambrose et al. reported the ionic liquid tagged Co(salen) with which veratryl alcohol was selectively oxidized to veratraldehyde using air or pure

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oxygen as the source of oxygen [16]. Metal [H₄]salen complexes showed higher activity than [H₂]salen complexes due to their more flexible C-N bonds [17]. In addition, they possess more activity and stability when encapsulated in zeolite or other supports [15]. In our laboratory, it was found that metal [H₄]salen complexes encapsulated in zeolite showed strong activity in catalytic oxidation of lignin [18]. Therefore, we are encouraged to extend metal [H₄]salen complex encapsulated in zeolite to the fast pyrolysis of Napier Grass. This work is hence wished to provide a new catalytic process in Napier grass pyrolysis.

EXPERIMENTAL SECTION

Napier grass

Napier grass samples were collected from a field in Kunming, Yunnan province. The stalks were cut into small pieces, washed with *deionized water*, vacuum-dried in an oven at 60 °C, and ground to obtain *powders*. The constituent and element of Napier grass were analysed as shown in Table 1.

Catalyst preparation

The NaY molecular sieve was activated by heating at 200 °C for 2 h in vacuum and then used to prepare encapsulated Cu([H₄]salen) and ([H₂]salen) complexes following a procedure described in our *previous study*, where the encapsulation of the complex into NaY was carried out by the impregnation (IM) method [19].

These neat and encapsulated complexes were successfully synthesized as characterized by XRD, FT-IR, DR UV-Vis, BET methods. The specific surface area, pore volume, pore diameter of the complexes were listed in Table 2.

Typical catalytic trials

The pyrolysis was performed in the fast pyrolysis equipment (Fig. 1). Napier grass powders were weighed and immersed in a aqueous solution containing catalysts, then mixed under stirring for 3 h, and finally vacuum-dried at 60 °C for the next pyrolysis. Nitrogen was introduced to form a fluidization in reactor, and then the reactor was heated to a definite temperature. Napier grass powders containing catalyst were pushed into the reactor. The powders was then rapidly pyrolyzed into vapour. Char and vapour were obtained through separation in the separator. The vapour from the separator passed into the condensator, and the bio-oil was obtained by cooling.

The calculation for the yield of bio-oil, char and gas in Napier grass pyrolysis was as follows:

$$\text{Bio-oil yield} = (\text{bio-oil mass}/\text{Napier grass mass}) \times 100 \%$$

$$\text{Char yield} = (\text{char mass}/\text{Napier grass mass}) \times 100 \%$$

$$\text{Gas yield} = (1 - \text{bio-oil yield} - \text{char yield}) \times 100 \%$$

Characterization of bio-oil

The content of water in bio-oil was measured using Mettler Toledo KF-V30 *moisture meter*.

Characterization of calorific value

Calorific value was measured using ZDHW-900C automatic calorimeter.

GC/MS

The bio-oil was detected using Agilent HP68 90-5973 GC-MS *equipped with* quartz capillary column (30 m × 0.25 mm × 0.25 μm); The following temperature programming was used in GC analysis: 40 °C (hold 5 min) → 180 °C (5 °C/min) → 280 °C (10 °C/min) hold for 3 min; carrier gas (He) 2mL/min; EI mode. Compounds were identified by comparing the mass spectra of the products with NIST standard spectra.

RESULTS AND DISCUSSION

Effect of catalysis on yield of bio-oil, char and gas

Temperature is an important factor affecting yield of pyrolysis products. In this work, the effect of temperature on the yield of pyrolysis products was studied, the results were shown in Fig. 2. It was found that the bio-oil yield increased with the increase of temperature, but decreased as temperature continued to rise. The cellulose content was higher and the lignin content was lower in Napier grass as a herbaceous plant than wood, the bio-oil yield in Napier grass pyrolysis was then lower. Therefore, it was needed to increase the bio-oil yield by using catalysis [20, 21].

Catalysis could reduce the activation energy of reaction, so that pyrolysis would occurred in a *range* of low temperature, which could improved biomass conversion [22]. Our study showed that the activity of Cu([H₄]salen) was higher than [H₂]salen complex due to the more flexible C-N bond. In addition, the encapsulation rendered Cu([H₄]salen) complex more active compared to the neat complex in lignin degradation [19].

Table 1: Chemical composition and element of Napier grass.

Composition (wt%)					Element(wt%)			
Cellulose	Hemicellulose	Lignin	Ash	Acetone extractives	C	H	O	N
38.82	30.37	22.56	2.84	5.28	44.47	6.51	36.35	0.17

Table 2: Characteristics of encapsulated Cu(II) [H4]salen and [H2]salen complexes.

Sample	S_{BET} ($m^2 g^{-1}$)	V_{BJH} ($cm^3 g^{-1}$)	D_{BJH} (nm)	D_{BET} (nm)
NaY	558.17	0.31	7.52	3.27
Cu([H ₂]salen)/IM	230.10	0.15	4.83	2.21
Cu([H ₄]salen)/IM	378.74	0.27	5.72	2.67

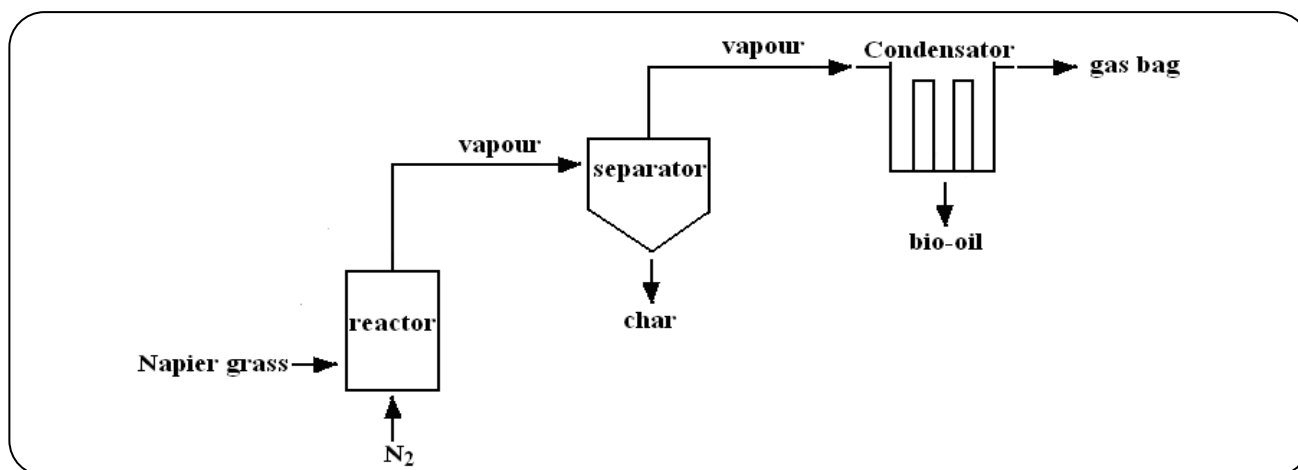


Fig. 1: Scheme of fast pyrolysis of Napier grass.

Consequently, the bio-oil yield increased (Fig. 2a) with the increasingly catalytic activity from NaY to Cu([H₄]salen)/IM.

Different pyrolysis temperatures also led to different char yields. According to Fig. 2b, the char yield decreased to the lowest value, and then flattened gradually. This can be explained by lignin *decomposition*. With temperature increasing, Napier grass pyrolysis and lignin degradation increased, which led to the decrease of the char yield as well. When lignin was almost degraded completely, little changes were not found in the char yield. In addition, the char yield and the corresponding temperature were relatively low during catalytic pyrolysis compared to the control (Fig. 2b), which was mainly due to the catalytic degradation of lignin in Napier grass pyrolysis [23].

In the range of low temperature used, the gas yield was relatively low due to the *insufficient* pyrolysis occurred in Napier grass, and significantly increased with temperature increasing (Fig. 2c) as a result of the acceleration of secondary pyrolysis.

It was shown from the data in Fig. 3 that the bio-oil yield increased when the pyrolysis time went from 0.2 s to 0.6 s. When the pyrolysis time increased from 0.6 s to 1.2 s, the secondary pyrolysis of Napier grass strengthened, some *large molecules* were cracked into small *molecules*, the bio-oil yield consequently decreased, the gas yield increased because of the increase of noncondensable gas. At the beginning of pyrolysis, Napier grass was degraded *insufficiently*, the condensation, cyclization and dehydroaromatization may occurred between *large molecules* in bio-oil, the char

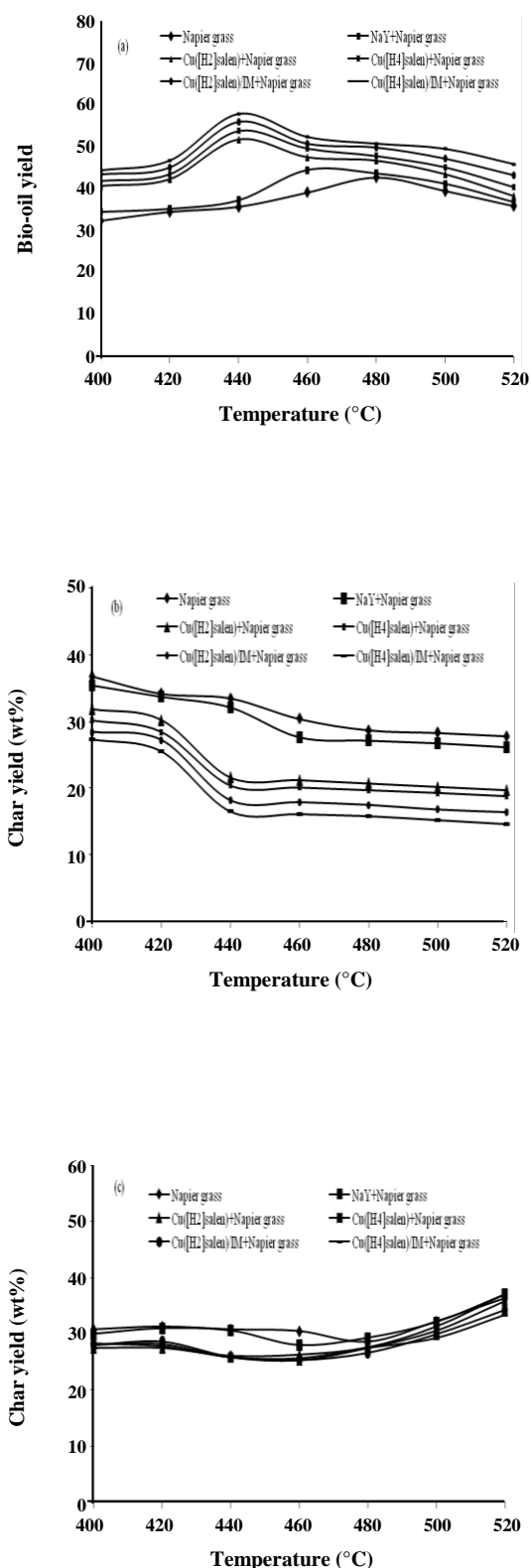


Fig. 2: Pyrolysis temperature vs yield of bio-oil (a), char (b) and gas (c). Retention time: 0.6 s; catalyst dosage: 6 %.

yield increased [24]. Following that the char yield decreased. Fig. 3 also showed that the catalysis produced more bio-oil, less char, but little effects were found on the production rate of gas in the pyrolysis of Napier grass.

It was also found that the yield of various pyrolysis products could be monitored by adjusting catalyst dosage. The bio-oil yield increased, and the char yield decreased with the catalyst dosage increasing (Fig. 4). When the catalyst dosage continued to increase, the bio-oil yield was tending towards stability. Therefore, it was appropriate that the catalyst dosage of 6 % was used in Napier grass pyrolysis in order to obtain maximum yield of bio-oil.

Effect of catalysis on composition and quality of bio-oil

It was shown as in Table 3 that the chemical composition of bio-oil included phenolics, ketones, hydrocarbon. The quality of bio-oil obtained by catalysis was significantly superior to that by uncatalysis. Catalysis enhanced the decomposition of lignin and thus the content of phenolics in bio-oil increased, which led to an increase in heating value of the bio-oil (Table 4) due to the high heating value of phenolics. The bio-oil obtained by catalysis contained low content of ketones. At the same time, oxygen in bio-oil was removed by catalytic pyrolysis as a form of H₂O₂, CO₂ or CO [25], which caused a fall of the content of ketones, 3,7,11,15-tetramethyl-1-ol-2-hexadecylene, N-palmitic acid and 9-hexadecenoic acid.

As shown in Table 4, the bio-oil obtained by catalysis contained oxygen in low content obviously compared to that obtained by uncatalysis. In addition, It was found that Cu([H₄]salen)/IM as a pyrolysis catalyst provided a deoxygenation from the bio-oil obviously compared to the data found in literatures [26-28].

In addition, the water content in bio-oil was considered to decrease with catalysis (Table 4) due to the catalysis resulting in the decrease of polycondensation occurred in pyrolysis process [29]. The catalytic effect was also found on the bio-oil pH. As shown in Table 4, the bio-oil pH was improved when catalysis was used in Napier grass pyrolysis, and it was found that the pH of bio-oil from Napier grass pyrolysis was higher than that from wood pyrolysis [30, 31]. Acids in bio-oil were mainly produced by hemicellulose pyrolysis and they were degraded to form small molecules, which could be strengthened by catalysis in pyrolysis process, and thereby increasing the bio-oil pH [32].

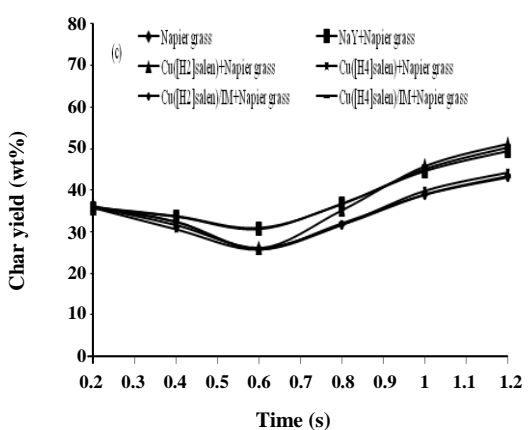
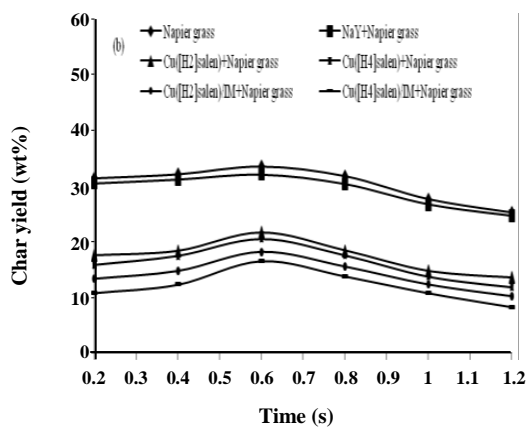
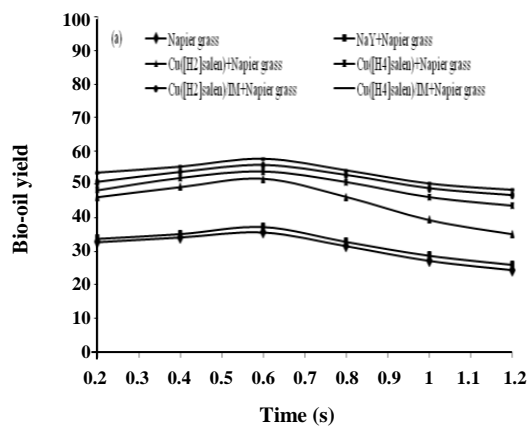


Fig. 3: Pyrolysis time vs yield of bio-oil (a), char (b) and gas (c). Temperature: 440 °C; catalyst dosage: 6 %.

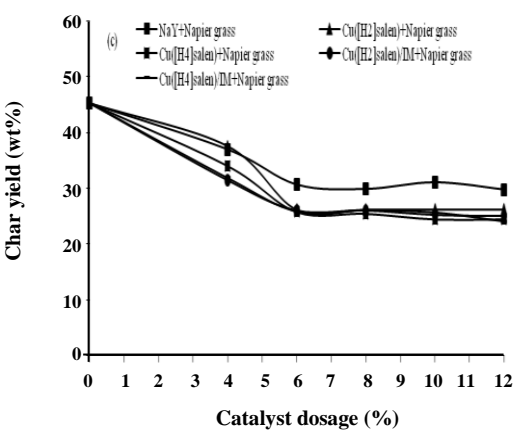
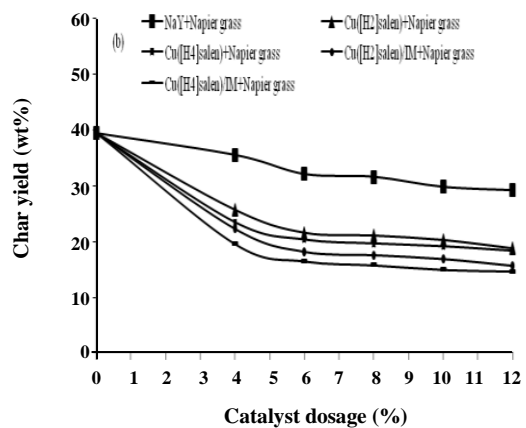
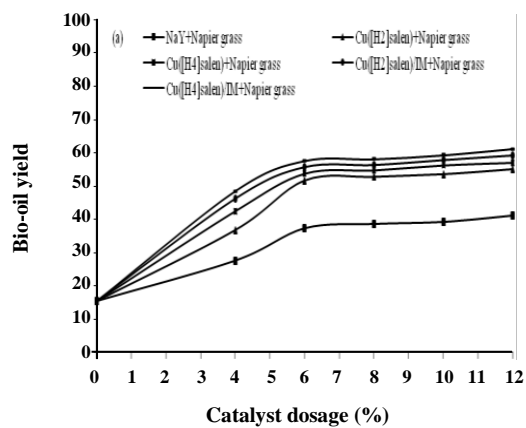


Fig. 4: Catalyst dosage vs yield of bio-oil (a), char (b) and gas (c). Retention time: 0.6 s; Temperature: 440 °C.

Table 3: Composition of bio-oil.

Phenolics	Ketones	Hdrocarbon
2-Methoxyl phenol	1-Hydroxyl-2- <i>acetone</i>	Bicyclo[4.2.0]octa-1,3,5-triene
4-Methyl phenol	4-Hydroxyl-2-methyl-2- <i>pentanone</i>	Styrene
2,3-Dimethyl phenol	Furanone	Dodecane
2,6-Dimethoxy phenol	3-Methyl-1,2- <i>cyclopentanone</i>	Tridecane
Phenol	4,4-Dimethoxy-2- <i>butanone</i>	Tetradecane
2-Hydroxyl phenol	<i>Dutanone</i>	<u>Pentadecane</u>
4-Ethyl-1,3-benzenediol	2,5-Dimethyl-4-hydroxyl-3(2H)-furanone	<u>Hexadecane</u>
Butylated hydroxytoluene	2,4-Dihydroxy-3-methoxy acetophenone	<u>Diocylmethane</u>
3-Methyl-1,2-dihydroxybenzene	4-Hydroxy-3-methoxyphenyl ethanone	
2-Methoxyl-4-propyl phenol	4-Hydroxy-3,5-dimethoxyphenyl ethanone	

Table 4: Quality of bio-oil obtained by different catalysis.

Catalysis	Phenolics (wt%)	Ketones (wt%)	Hdrocarbon (wt%)	C (wt%)	H (wt%)	O (wt%)	N (wt%)	Water content (wt%)	pH	Heating value (MJ kg ⁻¹)
Napier grass	12.3	17.7	2.2	61.84	7.71	23.22	7.23	15.2	3.1	14.6
NaY+Napier grass	14.5	16.2	2.8	62.59	9.23	20.16	8.02	14.1	3.3	15.4
Cu([H ₂]salen)+Napier grass	18.7	14.8	3.2	67.27	12.16	14.36	6.21	12.5	3.5	16.8
Cu([H ₄]salen)+Napier grass	21.2	12.8	3.9	69.05	13.76	10.72	6.47	11.2	3.7	18.2
Cu([H ₂]salen)/IM+Napier grass	23.4	10.9	4.7	72.76	15.38	4.73	7.13	9.1	4.3	19.4
Cu([H ₄]salen)/IM+Napier grass	25.5	8.7	6.2	74.13	17.29	2.17	6.41	8.3	5.1	22.7

CONCLUSIONS

Cu([H₄]salen) was synthesized by using a reduction reaction of [H₂]salen complex to obtain more flexible C-N bonds. By implementing the encapsulation of Cu([H₄]salen) on the NaY support, a more active and stable catalyst has been achieved in the fast pyrolysis of Napier grass compared to other catalysts, which would boost further production of bio-oil, and resulted in an increase in bio-oil quality.

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