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Steam Reforming of Biomass Tar Using Iron-based Catalysts

Elena David

National Research Institute of Cryogenics & Isotope Technologies, C.P.Râureni; P.O.Box 7, 240050 Rm.Valcea, Romania
elena.david@icsi.ro

Gasification of biomass is an important process for utilization of production of chemicals and fuels. During the gasification, biomass is converted with oxygen,air or steam into a gas mixture such as CO, CO_2, H_2, H_20 etc. Besides the gases, a number of low, volatile hydrocarbons (mostly CH_4) are obtained, together with tars. The tar represents a complex mixture of components, usually polyaromatic that are difficult to deal with in the downstream processes that accompany gasification as well as in utilization technologies. The gasification technology for biomass conversion is still in the development stage and cannot be considered as proven technology for small and medium scale applications. The main technical barrier remains the efficient removal of tar from the produced gases in gasification systems. The purpose of this work is to identify an appropriate catalyst that can be used as an active in-bed material for removal of biomass tar to increase the efficiency processing. Novel nano char-supported iron catalysts were prepared, tested for the steam reforming of biomass tar and their performances were compared with ilmenite catalyst. The activity of char-supported iron catalysts toward steam tar reforming process was investigated under different operational conditions. The experimental data show that catalysts have activity in steam tar reforming process. At low temperature, the tar was mainly converted into coke using iron carbon catalyst , whereas, at high temperature, the tar was primarily reformed into gas using ilmenite. The specific reactivity of the char-supported iron catalyst changed significantly after the steam reforming at different temperatures because of the changes in the properties of the char and the iron-containing species in the catalyst.

1. Introduction

Energy demand and global warming have become the most important problems due to increasing of the world population and economic and industrial activities. According to World Energy Outlook, the demand of world primary energy will increase by 45% between 2006 and 2030 at an average rate of 1.6% (IEA, 2008). The fossil can not satisfy the increase energy demand and their use will increase the CO_2 emissions. The utilization of coal can also generate other toxic compounds, that could seriously affect the local environment and people health. Lately, the biomass has become an increasingly renewable energy source because of its environmental benefits (Hassan, et al ., 2009). Among all renewable energy sources, biomass is considered the largest contributor to global primary energy supply and total world demand for biomass would rise (i.e. 1186 Mtoe in 2006 to about 1660 Mtoe by 2030) at an increase rate of 1.4% (IEA, 2008).

Compared with other renewable energy sources, biomass can be a substitute for all fossil-fuel-based products by a wide range of technologies that exist to convert the biomass into electricity, heat and liquid fuels (Gauthier et al., 2013). The gasification process of biomass represents an efficient way to generate energy with high efficiency and low environmental impacts. The biomass gasification process has a lot of difficulties and is not ready to become a commercial technology, the most important one is the presence of tar in the gaseous product. (Han and Kim 2008). Tar can cause the plugging of downstream equipments and also the poisoning of catalysts, resulting in a drop in efficiency as well as an increase in maintenance cost (Matsuhara et al., 2010). For these reasons, the removal has become an important way that should be considered to develop a biomass gasification technology. Generally, tar can potentially be removed from the gaseous

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products by physical separation processes (e.g. filtrations and scrubbing), thermal reforming and catalytic reforming processes (Han and Kim 2008). The catalytic reforming process is a good option, because it does not determine heat loss and can convert tar into syngas at the same temperature as gasifier efficiently . The catalysts are of two types, mineral and synthetic catalysts, based on their obtaining methods (De Caprariis et al., 2014). Various forms of iron have been reported as the catalysts used in tar decomposition (Azhar Uddin et al., 2008). Also , char has been used as catalyst in tar decomposition process , but the char can be consumed by gasification agents and gaseous products, such as steam, air or CO_2 (Abu El-Rub et al., 2008).Compared with dolomite, the activity of char is lower and is consumed due to gasification process. However, consumption of char would maintain its activity and tar removal by forming and generating micropores. Based on above , it can say many catalysts used in tar reforming still have a lots of problems such as: low activity, easy poisoning and deactivation, difficult regeneration, high cost, etc. Therefore, the investigating of the catalysts with low cost and high activity for tar reforming is very important and significant to commercialize biomass gasification technology. The purpose of the work was to investigate iron-based catalysts with low cost and high activity for the steam reforming of residual biomass tar. In addition I emphasize that large surface of the European countries among Romania include plains and hills, that are suitable for growing crops and trees(i.e. rape and walnut are among the most prevalent in this area). Rapeseed used to obtain bio-oil and nuts are widely used in food industry. Consequently, large quantities of rapeseed oil cake and shells result and proven to be an important residual biomass. Therefore, this residue has been chosen as feedstock in the study. Also, ilmenite is an abundant , it consists of iron oxides and titanium dioxides and is not expensive. Iron-containing species in ilmenite are dispersed well by titanium dioxides, which may result in its high possibilities to become the catalyst for tar reforming and it was also tested. Also, novel nano char-supported iron catalysts were prepared and tested in the steam reforming of biomass tar. Effects of support on the decomposition and reforming of tar were investigated.

2. Materials and methods

2.1. Pyrolysis process

The rapeseed oil cake (RSOC) and walnut shell (WS) used in this process. From RSOC and WS particles with size of about 150-200 μm was prepared a mixture in extruded form consisting of 1:1 w/w RSOC to WS. Two-stage fixed-bed reactors (horizontal and vertical reactors) were used . In first stage rapeseed oil cake/walnut shell mixture (RSOC/WS) was supposed to pyrolysis process and in the second stage the volatile matter (mainly tar) it was performed by catalytic steam reforming in situ.

The pyrolysis experiments were carried out under nitrogen atmosphere at a flow rate of 30 mL / sec and the reactor was one with fixed bed and made of stainless steel with 0.055 m diameter and 1m height. The reactor was placed in an electrical furnace and was heated externally. A quantity of 350 g of raw mixture (on a dry base) was loaded in reactor and in the pyrolysis reactor was placed a thermocouple to measure the temperature.

To remove the air, the reactor was purged by N_2 for 20 min at a flow rate of 30 mL/min and then the reactor temperature was increased at a heating rate of 5^{o}C /min up to desired pirolysis temperature. The temperature was maintained at the set value for 60 min. The pyrolysis temperature was varied between 500^{o}C and 850^{o}C.The N_2 removed all volatile components from the reactor and these were collected into the collection traps. The liquid product was condensed by cooling within water bath. From collection traps the tar was introduced in the second vertical reactor, at a rate tar/catalyst of 4:1 wt%.This reactor contains sand as bed material (250-400 μm).

The steam was generated by the water fed into the reactor .The steam flow rate was varied between 1.6 g/min and 8 g/min. The proximate analysis of rapeseed oil cake and walnut shells mixture and coal were done according to ASTM D3174-04 for ash analysis and ASTM D3175-89a for volatile matter. The ultimate analysis to determine the amounts of carbon, hydrogen, nitrogen, sulphur and oxygen (calculated by difference) was made in according to ASTM D5291-96 using a FLASH-2000 Elemental Analyzer. The gross calorific values were determined in according to ASTM D240-02.The proximate, ultimate and component analysis are presented in a previous work (David and Kopac, 2014). All chemicals used in the investigations were of analytical grade.

2.2. Catalyst preparation and tests

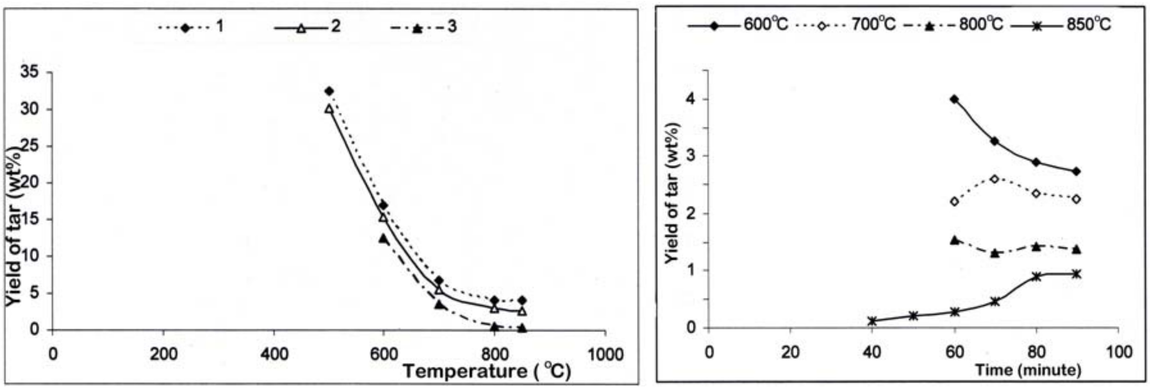
Brown coal provided of Petrila mine, Romania, was dried at room temperature for 12 h and then was pulverized and sieved . The size ranging from 63 to 177 μm was used as the catalyst precursor. The precursor was treated to remove the metallic species from coal. The coal was washed using an acid aqueous solution (0.25 M H_2SO_4) at a ratio of solution to coal 20:1 by mass and stirred in a nitrogen atmosphere for 16 h. The slurry was then filtered and washed with distilled water until a constant pH value(4.5-5.0). This coal sample was named as the H-form coal. The H-form coal sample was subjected to an ion exchange process using a 0.2 M $FeCl_3$ aqueous solution (a ratio of solution to coal 20:1 by mass) by stirring in a nitrogen atmosphere for 12 h to load iron into coal mass. The slurry was then filtered and washed using distilled water until a constant pH value(4.5-5.0) and finally the coal sample was dried in a nitrogen atmosphere, at 105^{O}C for 8 h. The treated coal was named as char-supported Fe catalyst. The iron content was 1.15wt% on dry basis and was determined by atomic absorption spectrometry method using an analyzer type Analytic Yena Nova 300. Also , the natural ilmenite ore was pulverized and sieved . The size ranging from 63 to 177 μm was used as catalyst in this study. The metal content and the proximate and ultimate analysis of ilmenite samples were determined using above mentioned methods. Ilmenite was used as catalyst for the steam reforming of volatiles from residual biomass directly and the results were compared to char-supported Fe catalyst. Before the steam reforming process to start, high purity hydrogen (99.99%) at a mass flow of 5 mL/s, was injected, into the first stage, to reduce ilmenite at 550^{O}C in situ for 60 minutes.Then, the H_2 feed was discontinued and the reactor was heated to the target temperature corresponding to the steam reforming tests (500-850 ^{O}C)

3. Results and discussion

Dolomites and olivine are natural minerals inexpensive and could be used to reform tar. The dolomites have shown good activity for tar decomposition (Han and Kim,2008), but they are fragile and a frequent replacement is required. Olivine has high attrition resistibility and to be used as catalyst need to be pretreated to obtain efficient activity for tar reforming and it is easy to be deactivated due to carbon deposition and to loss of iron dispersion.

3.1. Tar reforming on ilmenite catalyst and temperature influence and contact time

Ilmenite contains iron and titanium oxides, has high attrition resistibility and is widely present in natural ore. It is employed as catalyst in steam reforming of tar derived from the pyrolysis of RSOC/WS mixture in situ. The experimental data showed the temperature effect on steam reforming process. Figure 1a shows the tar yields of RSOC/WS mixture after reforming process with and without ilmenite at different temperatures.



(a) (b)

Figure 1. (a) - the tar yields of RSOC/WS mixture after pyrolysis and reforming without and with ilmenite catalyst at different temperatures(1-pyrolysis process; 2-reforming process without catalyst; 3-reforming process with ilmenite catalyst) and (b) - the coke yields of RSOC/WS mixture after reforming process with ilmenite at different temperatures.

It can be seen that all tar yields have decreased with the increasing of the temperature due to improved thermal cracking and reforming processes. The tar yields after pyrolysis process were similar to the results after reforming process without catalyst. This indicates that the steam has a little effect on thermal cracking process of tar in the gas phase , which is in agreement with the literature data (Li et al., 2009). Also, this behavior may be explained by the fact that large amounts of carbon dioxide and steam produced in the reactor bottom during pyrolysis process would have already reformed light compounds (i.e. oxygen-containing groups and aliphatics) in gaseous phase without the external steam.

As a consequence, it can say that is actually a self-reforming process, and the external steam may reform some light tar compounds, but the tar yields do not changes because of the low reactivity of heavy tar fraction, especially at lower temperature.

Accordingly, after pyrolysis process ,the tar yields were similar to results after the steam reforming without catalyst. There was clearly observed, when ilmenite was employed, the tar yields dropped and the tar adsorption on catalyst would extend the resident time and would result in the enhancement of thermal cracking and reforming processes. Most importantly, the reduction of tar on ilmenite catalyst is not only due to the extension of the resident time but also the active phase in ilmeinte catalyst.

The volatiles produced from the pyrolysis process contain abundant radicals which would react with tar molecules to form activated tar fragments by H- and CH_3- exception in the gas phase or/and on the ilmenite surface. These activated tar fragments could be reformed into gas by two ways on the surface of the catalyst(i.e. steam reforming and gasification). At lower temperature, the higher coke yields show that the coke formation is more significant than the steam reforming on ilmenite catalyst (Figure 1b). On the one hand, the molecules in the tar are large and the reactivity of steam is low at lower temperature.

The activated tar fragments could combine together easily on the surface of the ilmenite catalyst, resulting in higher coke deposits. At lower temperature, it can see that reaction rate of coke gasification is still weak , while a significant fraction of tar is transformed into coke. When the temperature increases, the molecules size in the tar decreases due to the improvement of the thermal cracking process, the reactivity of steam enhances, the activity of ilmenite catalyst improves and the reaction rate increases. All of these combine to cause lower tar yields.

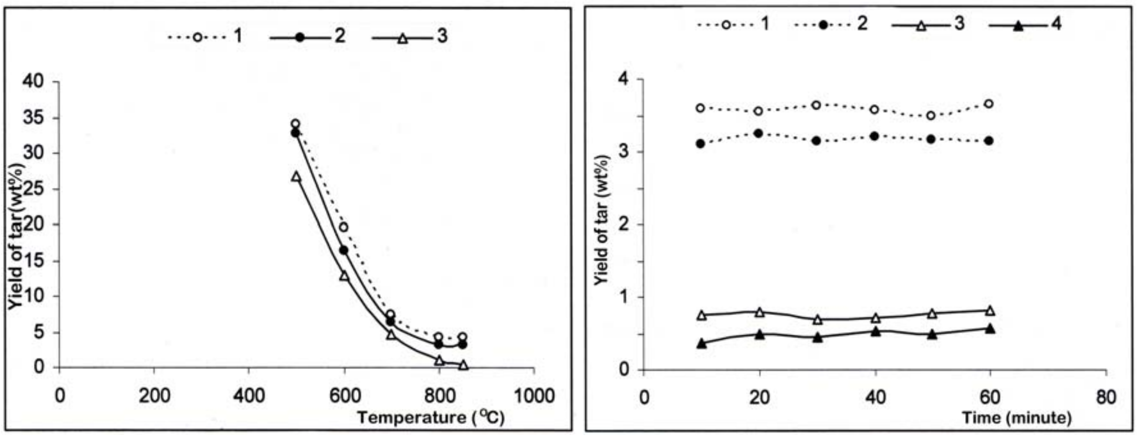
Aromatic compounds in the tar that could cause the coke deposits easily in downstream equipments are the major concern of gas composition and quality. The tar yields not always present the changes in aromatic composition because these are only a fraction of tar, this contain and other structures such as aliphatics, O-containing functional groups.

The above results show that externally added steam has little effects on the gas phase reforming of volatiles, especially at lower temperature, the role of the steam on reforming reaction, requires further researches and considerations. In special, role of the steam regarding to competitive reactions involving molecules or fragments adsorbed on catalyst, i.e. reforming into gas or polymerising into coke, need to be still studied and clarified. In order to enhance the performance of ilmenite catalyst for tar reforming process , the contact time was prolonged by increasing the mass of catalyst, while their properties (e.g. density, particle size) and the gas flow rate have remained unchanged. The contact times of amounts were 0.01 s, 0.02 s and 0.04 s, respectively.

The experimental data showed that tar conversion on ilmenite catalyst is higher than 70%. However, it is difficult to compare the results of steam reforming with amounts of ilmenite used because all data were low and in the range of experimental errors. The increase of the ilmenite catalyst mass prolonged the contact time, increased the total surface area and total active sites of the catalyst, which improved tar decomposition into gas on the catalyst.

3.2. Tar reforming on char-supported Fe catalyst, temperature influence and contact time

The performance of the catalyst on the steam reforming of the tar obtained by pyrolysis of RSOC/WS, under different operating parameters was analyzed. Figure 2a shows the tar yields obtained at different temperatures from volatiles by pyrolysis and steam reforming with/without char-supported Fe catalyst .



(a) (b)

Figure 2. (a) - Tar yields obtained from RSOC/WS mixture at different temperatures: 1-pyrolysis process; 2-reforming process without catalyst; 3-reforming process with the char-supported Fe catalyst and (b) - Tar yields obtained from RSOC/WS mixture for different times after reforming without/with the char-supported Fe catalyst (1-without catalyst and 800 ^{O}C; 2- without catalyst and 850 ^{O}C; 3-with char-supported Fe catalyst at 800 ^{O}C; 4- with char-supported Fe catalyst at 850 ^{O}C)

The tar yields after pyrolysis were similar to these after the steam reforming without catalyst. In agreement with literature (Azhar Uddin et al., 2008, Li and Suzuki , 2009), the addition steam has weak influences on the tar thermal cracking and reforming in the gaseous phase due to its low reactivity at lower temperature. However, when the temperature increased the tar yields decreased due to the improvement of thermal cracking and reforming processes. The H-form char catalyst prepared and tested presents some activity at higher temperature. In fact, the tar yields in steam reforming with char-supported Fe catalyst dropped towards steam reforming without catalyst. According to previous studies (Azhar Uddin et al., 2008), the iron clusters are nano particles with high dispersion into char mass and these give high catalytic activity. Although the effects of the char-supported Fe catalyst on the tar yields were difficult noted at lower temperature, its catalytic activity became very prominent at higher temperature (≥ 800^{O}C). The use of char-supported Fe catalyst determines about 82% till 95% reduction of the tar yield at 800^{O}C and 850^{O}C, respectively. Figure 2b presents the tar yields as time function. The tar yields in reforming with the char-supported Fe catalyst remains almost unchanged, from 10 to 60 minutes, demonstrating that the catalyst can keep its high activity for tar removal within the time range investigated.

3.3. The role of support in tar reforming process

The data obtained in experimental tests show that the char-supported Fe catalyst presents activity similar to that of the ilmenite catalyst at 800^{O}C and 850^{O}C, respectively. At lower temperature the activity is quite different. This behavior is related to the properties of the substrate. The catalyst support plays an important role on catalytic reaction. This statement is supported by the fact that ilmenite and the char-supported Fe catalyst showed different activities at lower temperature, although the catalysts have similar active phase consisting in iron species. The structural properties of char are favorable to the dehydrogenation and dehydration and the char not only disperses the iron-containing species but also interacts with the iron-containing species, that can improve its activity , especially at higher temperature. Compared with char, the surface of ilmenite contain large amounts of oxygen groups (e.g. TiO_2) which could be favorable to the stable adsorption of volatiles due to its polarity. These adsorbed molecules were combined together easily to form coke on the ilmenite at lower temperature due to the low reactivity of steam and the high thermal stability of aromatic ring systems. Instead, the heavy compounds (tar) in volatiles were difficulty adsorbed on the char surface due to its less oxygen groups and steric hindrance. In addition, huge amounts of radicals could be formed on the char surface from the char gasification, which may be favorable for the stabilization of the tar molecules. Thus, the tar molecules could pass through the catalyst bed easily, which resulted in the constant tar yields at low temperature (Figure 2b). Secondly and more significantly, at lower temperature, the porous structure and the surface properties of char support enhanced the dehydration and dehydrogenation reactions and lead to the increase of aromatic ring systems. The iron-containing species in catalyst exhibited much smaller particle size and higher dispersion than those in ilmenite, resulting in the extremely high activity of the char-supported iron catalyst at high temperature. Char acts not only as support but also as reducing agent for the catalyst. On the one hand, char, mainly acting as a support of the catalyst, similar to TiO_2 in ilmenite, can stop the agglomeration and diminish of the iron-containing species. Also, char interacts with the iron-containing species to produce reduced forms of iron which have high activity for the steam reforming of tar.

4. Conclusions

Ilmenite, a natural iron-containing mineral has exhibited activity for reforming tar during the steam reforming process. The highly dispersed iron-containing species in ilmenite contributed to its high and consistent activity and the function of TiO_2 is a support that could inhibit its sintering and agglomeration. The external steam had little effect on the thermal cracking and reforming of tar in the gas phase. However, it played an important role in the steam reforming of tar on ilmenite. Tar was mainly converted into coke on the catalyst at low temperature, whereas it was primarily reformed into gas on ilmenite at high temperature in the presence of the external steam. Tar was reformed efficiently on the char-supported catalyst during the steam reforming process. Compared with the ilmenite catalyst, the inexpensive char-supported Fe catalyst has significant advantages. The char-supported Fe catalyst maintains its activity within the time range investigated. The support proprieties significantly influenced the activities of the catalysts and the reaction pathways on the catalysts. Ilmenite and the char-supported Fe catalyst showed different activities although they included similar active phases.

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