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Biomass gasification in an atmospheric fluidised bed: Tar reduction with experimental iron-based granules from Höganäs AB, Sweden

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ABSTRACT

The present study investigates the effect of several experimental iron-based granules on biomass tar decomposition. The iron-based materials were provided by Höganäs AB and were all in their metallic state when they were applied in a secondary catalytic reactor. Bark-free birch was employed as fuel in an atmospheric fluidised bed reactor, and the tar concentration and gas composition in the producer gas were measured before and after the catalytic bed. The results demonstrate a clear tar reduction capacity for all the tested iron-based materials.

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1. Introduction

Thermochemical conversion by gasification of biomass is receiving increased attention as article potential source of renewable energy with respect to global issues of sustainable energy [1]. Gasification of biomass has several advantages compared to fossil fuels, which dramatically reduce the emission of CO_2 and other greenhouse gases [2]. Thermochemical treatment by gasification of biomass implies production of permanent gases such as CO_2, carbon monoxide (CO) hydrogen (H_2), and methane (CH_4). One of the major issues for an efficient gasification process is the formation of tars, which at temperatures below 350–400 °C may condense and cause plugging and corrosion in downstream process equipment. In addition, high levels of tars in the product gas may function as a poison for many downstream catalyst processes. Beside these problems, the tar also represents a not negligible energy loss, lowering the overall efficiency of the process.

One method to clean the gasification gas from tars is to use a secondary reactor containing a stationary catalytic bed. When passing the gas through the catalytic bed the tars, and also to some extent lighter hydrocarbons, are transformed into permanent gases. The requirements for a tar cracking catalyst is that it should be effective considering tar cracking, inexpensive, abundant and preferably conveying non-toxic deposals. It is readily reported and well established throughout the biomass gasification society that calcined dolomite ($Ca_xMg_{(1-x)}O$, $0 \leq x \leq 1$) meets these requirements [3–9]. However, in some cases the use of dolomite for tar cracking is not possible, e.g., when the biomass fuel contains high levels of chlorine, where the risk for catalyst depletion is impending due to reaction with chlorine-producing calcium chloride ($CaCl_2$) [10].

Iron-based catalyst materials have recently been reported to have tar cracking abilities [11]. These materials are less chlorine sensitive and have shown to also have a clear impact on the permanent gas composition [12]. The most effective tar cracking catalyst is still nickel [13,14]. However, this material may not be an alternative due to its higher costs.

In the present study a series of gasification experiment was conducted in a fluidised bed reactor at KTH. The aim was to explore the thermocatalytic tar reduction capacity of experimental iron-based granules. The campaign was performed in collaboration with the Swedish company Höganäs AB, who provided the iron granular materials. All the tested materials demonstrated tar reduction ability.

2. Experimental

2.1. Catalyst materials

Five types of iron materials (S, SDM, F, D and H) manufactured by Höganäs AB were tested for their ability to decompose tars. The metallic catalysts were characterised by means of Brunauer–Emmett–Teller (BET) surface area and elemental analysis.

The specific surface area were analysed by single point measurement with a Micromeritics Flowsorb III instrument according to the

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BET method using adsorption of N_2 at the temperature of liquid N_2. All the samples were degassed at 110 °C for 0.5 h before analysis. Elemental analysis of sulphur was carried out by using combustion analysis with a CS-400 LECO instrument. The concentration of oxygen and nitrogen was determined by an inert gas fusion principle with a TC-436 LECO instrument.

2.2. Experimental equipment

The KTH atmospheric fluidised bed gasification system consists of a biomass feeder, a pre-heater, a bubbling fluidised bed gasifier reactor, a ceramic filter and a catalytic bed reactor. A detailed experimental setup has been described by Nordgreen et al. [15].

The biomass fed to the gasifier reactor was Swedish birch (bark-free) with moisture content of approximately 8 wt%. Four hundred grams of biomass was loaded in the fuel hopper. This amount of fuel is sufficient for an operating time of about 100 min, which is enough to establish stable isothermal conditions and to avoid pronounced catalytic tar cracking effects in the filter vessel. The fuel, with a particle size of 1–1.5 mm, is fed directly into the fluidised bed near the distribution plate with aid of a screw feeder. The fuel hopper is provided with a purge gas of nitrogen and a cooling system to prevent hot gases from entering the hopper and making the fuel sticky. After each experiment, the remaining weights of biomass and bed material, respectively, were measured in order to calculate the char content and feeding rate.

Before the fluidisation media enters the reactor it is preheated to a temperature of 650 °C. The fluidised bed material consisted of 350 g alumina with a particle size of 63–125 μm. The fluidisation media is nitrogen and the oxidising agent is pure oxygen. The total flow of nitrogen and oxygen was 9.5 $dm^3(n)$/min and 0.65 $dm^3(n)$/min, respectively; this composition resulted in a lambda value of approximately 0.20. The gasification temperature was 850 °C in all experiments.

One hundred fifty grams of metallic iron were introduced in the catalyst container. The particle size was in the range of 1 to 3 mm. The temperatures in the catalytic bed were 750, 800 and 850 °C in the experiments. The experiments were all carried out in the same way starting with 750 °C followed by 800 °C and ending with 850 °C.

To analyse possible reduction of tars due to thermal cracking, experiments using an empty catalytic reactor were carried out at the same reactor temperatures as for the catalyst experiment. The results from these experiments were used to determine the tar reduction due to the catalytic effect of the iron materials.

The cool, dry, clean gas composition was analysed with a gas chromatograph (Model Shimadzu, Japan), equipped with a flame ionization detector (FID) and a thermal conductivity detector (TCD). The tar sampling and analysis was accomplished using the solid phase adsorption (SPA) method, described elsewhere [16]. Briefly, a 100 ml gas sample was manually drawn through a SPE tube during one minute. Later the SPE tubes were eluted using two different solvent mixtures to obtain an aromatic fraction and a phenolic fraction. The eluates were afterwards analysed by gas chromatography.

3. Results and discussion

3.1. Catalyst characterisation

The metallic catalysts were characterised with respect to BET surface area, porosity, chemical composition and morphology. The results are presented in Table 1. The three iron materials (S, SDM and F) have a oxygen content less than 0.8% and a BET surface area between 185 and 285 m^2/kg. The two last catalysts D and H differ from the other three in having higher oxygen contents 3.4 and 7.5%, respectively. Material H has also a much larger surface areas of 1700 m^2/kg.

Table 1
Characterisation of the iron based catalysts.

Catalyst materials	N%	O%	S%	BET area (m^2/kg)
S	0.013	0.762	0.005	185
SDM	0.000	0.367	0.002	281
F	0.000	0.801	0.001	285
D	0.001	3.40	0.002	360
H	0.010	7.50	0.003	1700

3.2. Tar reduction

Decomposition of tars occurs mainly due to thermal and catalytic effects. The catalytic reduction includes steam and dry reforming. The main reactions are shown below:

$$\text{Thermalconversion}: \quad pC_nH_x \leftrightarrow qC_mH_y + rH_2 \qquad (1)$$

$$\text{Catalyticsteamreforming}: \quad C_nH_x + nH_2O \leftrightarrow (n + x/2)H_2 + nCO(2)$$

$$\text{Catalyticdryreforming}: \quad C_nH_x + nCO_2 \leftrightarrow (x/2)H_2 + 2nCO \qquad (3)$$

C_nH_x represents tar, and C_mH_y represents hydrocarbon with smaller carbon number than C_nH_x.

The main components in the tar formed in high-temperature gasification of biomass are naphthalene, toluene, indane and indene and some C_{18+} hydrocarbons. The molecular weight of the chromatographically tars are in the range of 78–202 g/mol. The typical tar composition (%) in the raw gas after the filter at the gasification temperature 850 °C is presented in Table 2.

In the present study, two types of experiments were performed: catalytic and thermal tar reduction. The thermal cracking experiments were performed in an empty catalytic reactor at the temperatures 750, 800 and 850 °C with a gasification temperature of 850 °C.

Results from the thermocatalytic reduction of naphthalene (the main component, constituting about 50–70% of total tar) in the gasification gas are presented in Fig. 1. Naphthalene is considered to be the most difficult tar to be decomposed by catalytic decomposition [17] and normally is pronounced reduction effects observed only at higher temperatures >850 °C. This is also the case for the present study where the result shows that the naphthalene reduction capacity is most pronounced at 850 °C for all five iron materials employed. F, D and H materials have the highest activity for naphthalene decomposition. The thermal conversion increased from 3% at the temperature 750 °C to 32% at 850 °C. At the highest temperature, 850 °C in the catalytic bed, the catalytic reduction for F and D materials is around 40%, which is more than the thermal conversion. Material F has also the highest catalytic activity for reduction (21%) at the lowest catalytic bed temperature of 750 °C. The thermal conversion is around 3% at this temperature.

It is clear from the results that naphthalene reduction is not dependent on the surface area of the different materials. This is

Table 2
Tar composition in the product gas before the catalytic bed (%).

Naphthalene	58.7
Phenanthrene	6.6
Indene	6.1
Indan	5.4
Acenaphthylene	5.5
Toluene	3.8
Fluorantene	3.4
Pyrene	3.0
2-Methylnaphthalene	2.9
Other	4.6

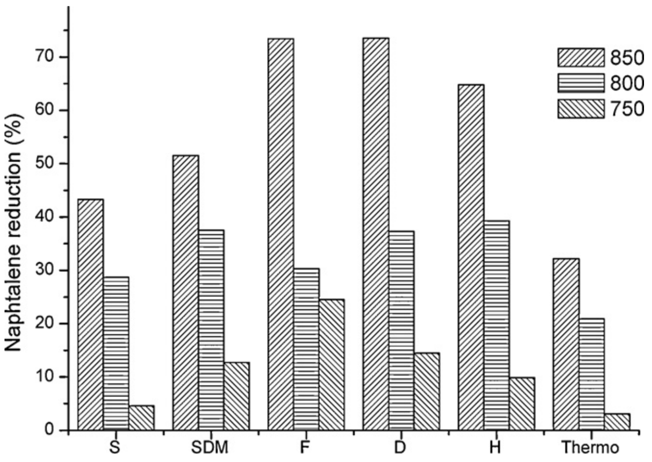

Fig. 1. Thermocatalytic reduction of naphthalene at different catalytic bed temperatures for the five catalyst materials. The effect of thermal conversion is included to the right. Gasification temperature $T = 850\,^{\circ}$C.

illustrated by F, D and H with similar reduction capacity at 850 °C, but with very large differences in surface area of 285, 360 and 1700, respectively.

Since the highest tar reducing capacity is expected for a pure metallic iron material, a lower activity can be assumed for the materials with higher oxygen content, i.e. H and D. This may be true if one considers the results at 750 °C where the reduction capacity follows the order F > D > H. The oxygen content are 0.8, 3.4 and 7.5 for F, D and H, respectively. Interesting to note is the shift in reduction trend at the 800 °C, where the order is the opposite, i.e. H > D > F. The reason for this change is not easy to explain, but could perhaps be due to a shift from one rate-determining reaction to another. A clear mechanistic picture is not possible due to the lack of comprehensible results. However, other possible tar reduction pathways can be suggested. For instance, in addition to naphthalene reduction governed by catalytic decomposition on pure metallic iron, the oxidative decomposition on iron oxide [18] is also a possibility for the materials with high oxygen content. This process requires free oxygen, which may be available in form of loosely bonded oxygen or free dissolved in the oxide matrix in the material. Since no other oxygen is supplied from the outside the source is limited and the process will therefore decline and disappear in time.

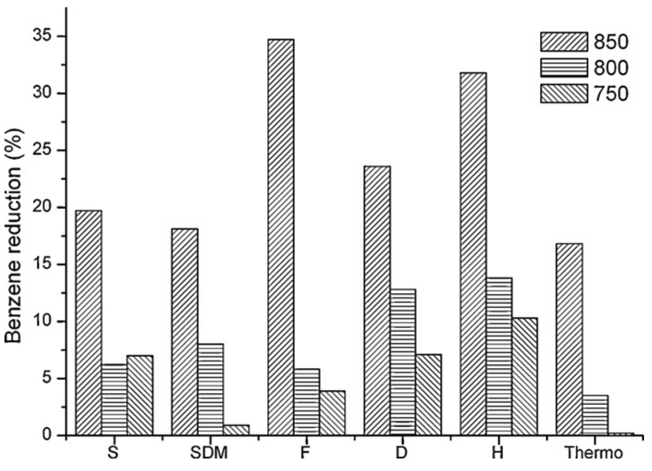

Fig. 2. Benzene reduction at different catalytic bed temperatures for the five catalyst materials. The effect of thermal conversion is included to the right. Gasification temperature T=850 °C.

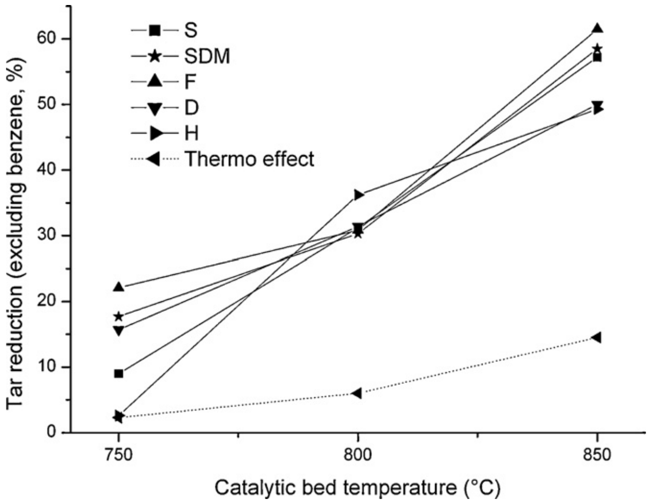

Fig. 3. Results of total tar reduction for different types of iron-based materials at different temperatures in the catalytic bed (gasification temperature is 850 °C).

The results for benzene reduction, presented in Fig. 2, follow in many cases the same pattern as the case of naphthalene. Benzene is not counted as a tar but since the catalyst has a pronounced effect on the benzene reduction, a survey of its existence in different operational situations is needed. Benzene is also an important product and intermediate in the complex tar reaction network of cracking heavier tars.

Also in this case, the materials F, D and H display the highest catalytic effect at 850 °C although material D is lower than the other two, slightly larger than S and SDM. The trend in benzene reduction at 750 °C is opposite, increasing from F to H, compared to naphthalene reduction. Material F shows the highest thermocatalytic reduction (when catalytic bed temperature was 850 °C)–34.7%, where 16.8% is due to the thermal effect and 17.9% catalytic reforming. The materials S and SDM have a capacity to reduce benzene, around 20%, which means a catalytic reduction of only 3%. At the low catalytic bed temperatures 800 and 750 °C the catalytic reduction is between 1 and 6% for S, SDM and F materials, whereas H and D catalytically reduced benzene by 10%.

The total tar thermocatalytic reduction (excluding benzene) may also be illustrated in terms of percentage of tar reduction as shown in Fig. 3. From the plot it can be seen that the thermal effect increases from 2 to 15% with increasing temperature. At the same time the catalytic effect increases from 10–20% to 35–45% with increasing temperature. The thermal reduction is in general between 10 and 20% of the total tar conversion. The greatest tar thermocatalytic reduction capacity, about 60%, is obtained with materials F, S and SDM (almost oxygen-free materials), whereas material H and D (oxygen-rich catalysts) demonstrate a slightly lower capacity of approximately 50%.

The obtained lower total tar reduction for H and D may be due to their higher content of oxygen. However, in view of their high naphthalene reduction capacity, the low total tar reduction may be due to the formation of other aromatic and polyaromatic hydrocarbons. This has been proposed by Devi et al. [17], investigating the decomposition of naphthalene over a pre-treated olivine catalyst. That work proposed a complex reaction network with formation of several side-reactions, for instance, indene, toluene, acenaphthalene, crysene and other polyaromatic hydrocarbons. This may explain the simultaneous high naphthalene and low total tar reduction for the D and H materials. The tar content in the gasification gas before the catalytic bed is about 3.9 mg/g biomass. The benzene content is about 10.1 mg/g biomass. After the catalytic bed, the tar content is reduced to about 1.3 mg/g biomass for the most effective iron materials (F, S and SDM). This corresponds to approximately 400 mg/Nm^3.

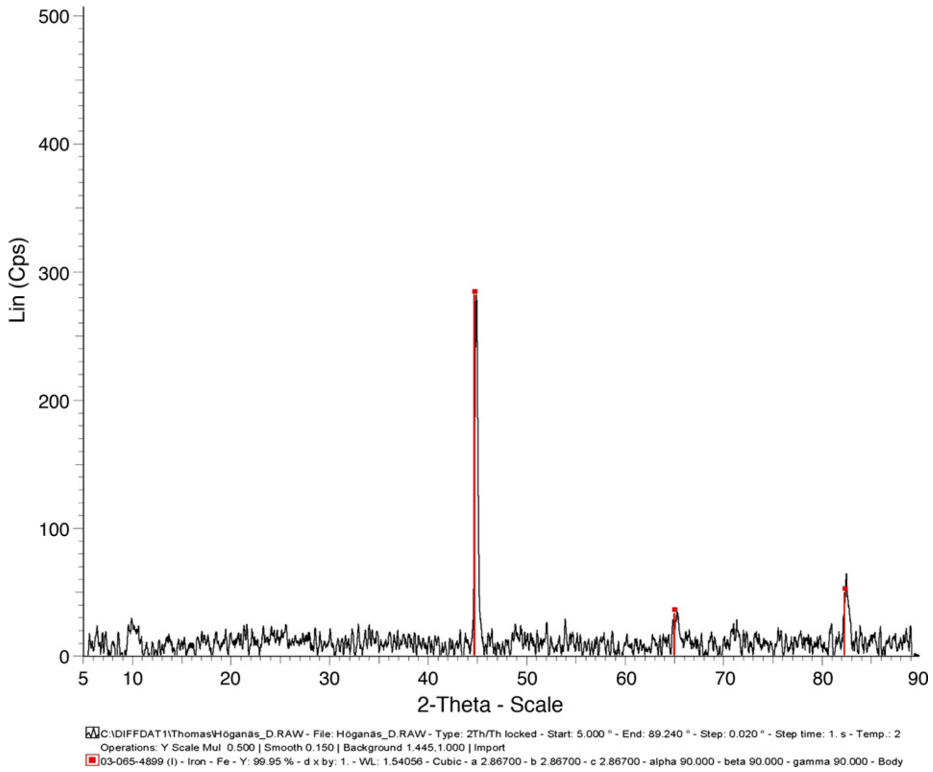

Fig. 4. XRD result for iron material D.

The presence of a metallic state of the iron materials is supported by XRD examinations as illustrated in Fig. 4 for material D. The XRD examination, clearly displaying a distinguished peak for pure iron, was carried out on a sample after use in the catalytic bed.

3.3. *Gas production*

The concentration of the main gas components CO, CO_2, H_2, and CH_4 were measured before and after the catalytic bed. Fig. 5 presents the gas yield, the volume of gas produced per amount of biomass converted, at different temperatures in the catalytic bed.

In Fig. 5, it can be seen that the gas yield increases when the temperature is increasing in the catalytic bed. This increase may be due to the conversion (both thermal and catalytic) of tars into gaseous components, adding up to the gas flow. Clearly distinguished is the pronounced effect for material F at the higher temperatures.

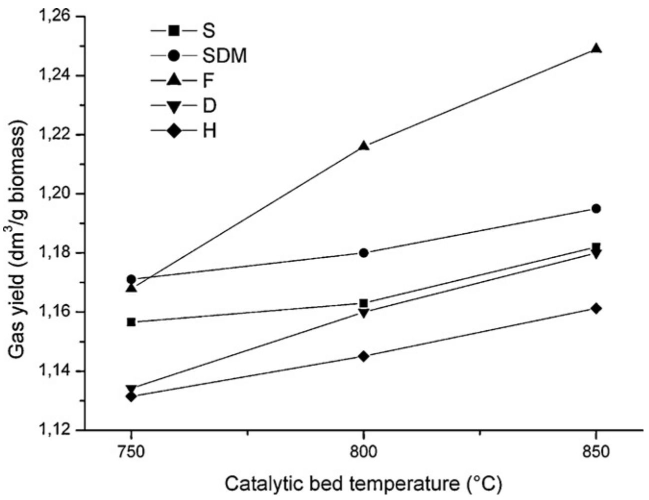

Fig. 5. Gas yield at different catalytic bed temperatures. The temperature in the fluidised bed is 850 °C.

At a catalytic temperature of 850 °C only small fluctuations in the gas composition could be observed after applying the different iron granules in the catalytic bed. Typical values for the gas composition are: 7% CH_4, 22% CO_2, 26% H_2 and 43% CO.

4. Concluding points

Experimental iron-based granules (S, SDM, F, D and H) manufactured by Höganäs AB were tested for their ability to decompose tars.

The metallic catalysts were characterised regarding their BET surface area and elemental composition.

Both catalytic and thermal tar reduction were examined.

The thermal reduction capacity is in general between 10 and 20% of the total tar conversion.

The greatest thermocatalytic tar reduction, about 60%, is obtained with material F, S and SDM whereas material H and D demonstrate a slightly lower capacity.

The lower tar cracking capacity for D and H is probably due to their higher oxygen content, i.e. higher content of stable iron oxides.

The gas yield is increased at increasing temperature in the catalytic bed. This increase may be due to the conversion (both thermal and catalytic) of tars into gaseous components.

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