

Tar formation, Reduction and Technology of Tar during Biomass Gasification/ Pyrolysis – an Overview

Naveen Kumar Pattar*, Gowreesh S S#
PG Student*, M. Tech Thermal Engineering,
Associate Professor#,
Department of Mechanical Engineering,
JSSATE, Bangalore., VTU Belgaum.

Abstract - Biomass is an important primary energy source as well as renewable energy source. As the most promising biomass utilization method, gasification/pyrolysis produces not only useful fuel gases, char and chemicals, but also some byproducts like fly ash, NO_x, SO₂ and tar. Tar in the product gases will condense at low temperature, and lead to thickened or blockage in fuel lines, filters and engines. Moreover, too much tar in product gases will reduce the utilization efficiency of biomass. Therefore, the reduction or decomposition of tar in biomass derived fuel gases is one of the biggest obstacles in its utilization for power generation. In this paper, we review the literatures pertaining tar formation, reduction and technology of tar during pyrolysis also tar reduction or destruction methods during biomass gasification/pyrolysis. On the basis of their characteristics, the current tar reduction or destruction methods can be broadly divided into five main groups: mechanism methods, self-modification, thermal cracking, catalyst cracking and plasma methods.

1. INTRODUCTION

It is well known that biomass is one of the important primary and renewable energy sources. Moreover, biomass is neutral in carbon dioxide circulation, that is, the amount of carbon dioxide it consumed through photosynthesis is the same as that given off by combustion. With the depletion of fossil fuel sources as well as the global warming issues, the utilization of biomass has been more and more concerned. At present, biomass share in world's total primary energy consumption is about 12%, as shown in Fig. 1. It is estimated that biomass share will be increased to near 15% by 2010 in developed countries.

The gasification/pyrolysis for producing syngas is regarded as one of the most promising options for utilizing biomass. The syngas from biomass can be not only directly used in gas turbine for power generation but also catalytically converted into methanol, dimethyl ether, Fischer-Tropsch oils or other chemical products. Research into the gasification of carbonaceous fuels has traditionally focused on the reactions between solid fuels (e.g. coal, char and biomass) and gaseous reactants (e.g. O₂, CO₂, H₂O and H₂). The follow-up reactions that occur after the initial gasification reaction take place between gaseous, or in some cases liquid, products. There is a significant amount of information available on these reactions, such as the water-gas-shift reaction ($H_2 + CO_2 \rightarrow$

$H_2O + CO$) and the methane reforming reaction ($CH_4 + H_2O \rightarrow CO + 3 H_2$). Some other reactions, however, have attracted less attention in the past, as they are relatively unimportant in coal and char gasification: for example, the reaction (gasification or separation) of tar compounds, which is particularly important in biomass gasification. This has been an increasing area of research during the past decade because of the growing demand for a sustainable energy supply and more recently because of the desire to reduce greenhouse gas emissions.

Although plenty of studies have previously been carried out into decomposition reactions of biomass tars and the formation of tars in the hydro pyrolysis and hydrogasification of biomass, this information is not readily accessible.

In the gasification/pyrolysis process, with exception of generating useful products, many byproducts such as fly ash, NO_x, SO₂ and tar are also formed. Tar derived from biomass gasification or pyrolysis will be condensed as temperature is lower than its dew point, then block and foul process equipment's like fuel lines, filters, engines and turbines. It was reported that tar content in the syngas from an air-blown circulating fluidized bed(CFB) biomass gasifier was about 10 g/m³. For other types of gasifier, tar content varied from about 0.5 to 100 g/m³. However, most applications of product gases require a low tar content, of the order 0.05 g/m³ or less. Hence, tar disposal becomes one of the most necessary and urgent problems during biomass gasification. Up to now, a great amount of

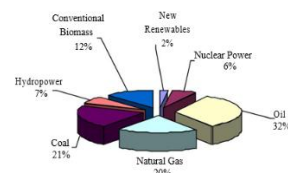


Fig. 1. The shares of current world's primary energy consumption.

work concerning tar reduction or reforming has been reported. In this work, we reviewed a great amount of literature and broadly divided the tar removal technologies into five groups: mechanism methods like cyclone, filters (baffle, fabric, ceramic), granular beds, RPS, Electrostatic precipitators and Scrubbers; self-modification, selecting optimal operation parameters for gasifier or using a low tar gasifier; Catalytic cracking; Thermal cracking and Plasma methods (Pyro arc, Corona, Glidarc).

1.1 Definition of tars and measuring techniques

This paper uses a number of terms and definitions that require some explanation or need to be defined first. Even the word 'tars' is far from unambiguous, as set out below.

□ Definition of tars and measuring techniques

For a discussion of the definition of tars and measuring techniques the reader is referred to an ECN report, No. C--04-014. In this report a conglomerate of Dutch research institutes and universities have developed a new classification system for tars and this is explained in detail. However, this standard is not universally used and therefore other definitions are also applicable.

In the case of the present report it is important to note that comparing data on tar concentrations and conversion from different studies is hampered by the fact that they use different definitions of tars and different methods of analyzing them. Often the definition of tars used is a practical one, based on the method used to measure them, e.g.:

'condensable tars' at temperature X
'tars that are soluble in solvent Y'

The present report sometimes compares data from different studies, e.g. on tar cracking under inert conditions, in CO₂/H₂O and in H₂. The author estimates that the data from the various studies are broadly comparable, without considering the definitions and measuring techniques in detail: for more details on these the reader is referred to the original articles. When, in the author's estimation, the measuring technique or definition of tars rules out even a broad comparison of data from different studies, this will be mentioned.

1. Primary, secondary and tertiary tars

The terms 'primary', 'secondary', 'tertiary', 'primary reactions' and 'secondary reactions' are not used uniformly in the literature. The term 'secondary tar' is particularly confusing, referring in some studies to the products of secondary reactions (i.e. all tars other than primary tars) and in others to an intermediate category of tars (between primary and tertiary tars).

This study uses definitions that can be regarded as a compromise between the commonly used terms 'primary reactions' and 'secondary reactions' and the definitions of 'primary', 'secondary' and 'tertiary' tars used in the studies by Evans and Milne, as they relate their definitions to actual compounds. They do not give names for the follow-up reactions, however. Also, we have retained the term 'secondary reactions' as it is in common use.

The compositions of the three types of tar given in are:
Primary products characterized by compounds derived from cellulose, hemicellulose or lignin, e.g. laevoglucose, hydroxyl acetaldehyde, furfurals and methoxy phenols

Secondary products characterized by phenols and olefins

Tertiary products characterized by aromatic compounds without oxygen substituents, divided into:
Alkalisated tertiary products, including methyl derivatives of the aromatics, e.g. methylacnaphthylene, methylnaphthalene, toluene and indene 'Condensed'

(simplified) tertiary products, i.e. the AHs/PAHs without substituents, e.g. benzene, naphthalene, acenaphthylene, anthracene, phenanthrene and pyrene

The two reactions are not linked to these three types of tar:

- (1) Primary reactions are those where biomass decomposes, generating tar compounds (primary tar). Pyrolysis oil or bio-oil is largely made up of primary tars, with some secondary tars
- (2) Secondary reactions are the continued reactions of the primary tar and can take place

both in the interior of the biomass particle and outside it, in the gas phase. Note that secondary reactions produce not only secondary but also tertiary tars

1 Thermal cracking, heterogeneous thermal cracking and catalytic cracking

In this study, cracking in the absence of a solid (i.e. in an empty, inert reactor) is referred to as 'thermal'. In the presence of an inert solid it is referred to as 'heterogeneous thermal', and in the presence of an active solid as 'catalytic'. Coal or char (such as activated carbon, anthracite, pyrolysis char, char in gasification ash) is regarded in this study as a catalyst (at high temperatures above 600°C) and also as a possible adsorbent (especially at low temperatures below 600°C). The 600°C dividing line is fairly arbitrary but probably lies in a region where the coal or char is not very active as a catalyst and does not adsorb tars to any significant extent.

2 Decomposition reactions, thermal cracking, gasification, hydrogasification

This report refers as consistently as possible to reactions of tars at high temperatures in general as 'tar decomposition reactions'. The terms 'thermal cracking' and 'gasification' are used for decomposition reactions in an inert atmosphere and in the presence of O₂ (in a limited amount), CO₂, H₂O and H₂ respectively. Tar combustion reactions (with excess O₂) are not considered in this report. For the specific reaction of tars with H₂ the term 'hydrogasification' is used. The difference between hydro pyrolysis and hydrogasification is explained in 3.5.1.

3 Carbon/char/coke/dust/soot

In this report the solid carbonaceous product of the thermal cracking of tars is referred to as 'carbon'. This is only one of the many possible nomenclatures: others used in the literature is char, coke, 'carbone' (French), dust, soot and 'pyrocarbon'.

2 MECHANISM METHODS

Mechanism methods include scrubber, filter, cyclone and electrostatic precipitator. The primary use of these devices is to capture particles from the product gases. A great amount of experimental results demonstrated that the methods were also considerably efficient in removing tar accompanied with effective particles capture. Tar separation efficiency ranging from 51% to 91% had been reported in a venturi scrubber used to purify the product gases from a countercurrent rice husk gasifier. Bridgewater

claimed that tar concentration in the fuel gases was lower than 20–40 mg/Nm³ after a high-efficient scrubber system.

A so-called RPS (rotating particle separator) was used in Energy Research Center of Netherlands(ECN) with an attempt to remove tar from product gases, but the results was unsatisfactory. Another new tar removal system called OLGA (“OLGA” is the Dutch acronym for oil-based gas washer) was also developed by Boerrigter in ECN. The OLGA had been successfully demonstrated in a laboratory scale biomass gasifier. The results indicated that tar could be selectively removed from the product gases without affecting the main gaseous products. In the OLGA, heavy tars were completely removed, which resulted in the dew point decrease, even lower than 25 °C. Therefore, tar would not condense at the downstream of gasifier. Furthermore, 99% phenol and 97% heterocyclic tars removal can be achieved, which was expected to be high enough to prevent excessive waste water treatment cost due to the pollution with phenol or other water-soluble tar compounds.

Electrostatic precipitation(ESP) is one of the primary particle collection devices in coal fired power plant, metallurgical industry and cement industry due to its high efficiency. It is declared by Paasen that more than 99% dust and 40–70% tar removal can be obtained by the ESP at an updraft gasifier in Harboore, a downdraft gasifier at Wiener Neustadt and a circulating fluidized bed gasifier at ECN. After passing ESP, the heavy tars in product gases were completely removed and the dew point of tar ranged from 130 to 21°C, which was sufficiently low for preventing the condensation of tar. Based on visual inspection, the author claimed that fouling at the ESP collector plates was negligible. Moreover, it was found that tar removal was not sensitive to the voltage and residence time.

Dinkelbach also experimentally studied wet ESP used in a Wellmann gasifier in Birmingham (UK). In the system, no operation problem had been found for a long term and the operators claimed to have obtained good “tar” separation efficiencies. Unfortunately, no detailed experimental data was available in the paper. The validity of ESP capturing tar was also confirmed by Neeft.

Activated carbon is a highly efficient sorbent, and is widely used to control a number of gaseous pollutions emission. Hasler investigated the possibility of using activated carbon granular bed filter to remove tar. The activated carbon filter was installed in the front of a fabric filter. In the experiments, the removal efficiencies for high boiling hydrocarbons and phenols were relative high. Meanwhile, the ‘tar’ laden activated carbon can be recycled as an extra feedstock. Hermann studied a pre-coated fabric filter used to remove particles and tar at a gasifier plant in Austria. The filter had been tested for more than 2500 h without any problems. The disadvantages of the filters were the following: the tar deposited in filter could not be easily cleaned; tar accumulation on the filter surface would lead to eventual plugging. Generally, barrier filters were not suitable for tar removal even though the filters were successfully demonstrated in some cases.

Hasler summarized the tar and particle reduction efficiency by various mechanism methods in Table 1.

As we know, the operating parameters play a very important role in the distribution of products during biomass gasification. The important parameters include temperature,

Table 1
 The reduction efficiency of particle and tar in various gas cleaning system

	Particle reduction (%)	Tar reduction (%)
		50
		–
Sand bed filter	70–99	97
		10
		–
Wash tower	60–98	25
		50
		–
Venturi scrubber		90
Wet electrostatic precipitator	499	0–60
		0–50
Fabric filter	70–95	30
		–
Rotational particle separator	85–90	70
Fixed bed tar adsorber		50

equivalence ratio (ER), the type of biomass, pressure, gasifying medium and residence time etc. Certainly, the selection of parameters also depends on the type of gasifier.

Researchers have conducted extensive studies concerning the influence of temperature on tar production during biomass gasification. Li reported that tar yield from biomass gasification decreased drastically from 15 to 0.54 g/Nm³ as the average temperature increased from 970 to 1090 K. NarvPaez also studied biomass gasification at different temperatures and found that the tar content at 700 and 800 1C were 19 and 5 g/Nm³, respectively. In the experiments of Fagbemi, tar yield was increased with the enhancement of temperature until to 600 1C, and then dropped with temperature increment. The phenomena can be explained the reasons: when the temperature was higher than 600 1C, the secondary reaction (i.e. tar cracking) prevailed, which led to tar decomposition.

Similar to temperature, Equivalence ratio(ER) increase also has a beneficial effect on reducing tar formation. However, the heat value of product gases will decrease with enhancing ER. Lv divided the biomass gasification into two stages based on the ER. In the first stage, ER varied from 0.19 to 0.23. When ER shifted from 0.19 to 0.23, gas yield also was increased from 2.13 to 2.37 Nm³/(kg biomass) and gas low heat value(LHV) was increased from 8817 to 8839 kJ/Nm³. The ER range of the

second stage was 0.23–0.27. In the stage, gas LHV decreased with ER increment because of strengthening oxidization reactions of product gases. Garca-Ibanez reported that the maximum amount of H₂ (9.3 vol%) occurred at an ER of 0.59 and ER had slight effect on the hydrocarbons content at the ER range of 0.59–0.73.

Kostrin investigated the relation of maximum tar yield with the type of biomass through experiments. It was obtained that the highest yield of tar was 35% for wood, around 60% for paper and only 30% for sawdust. A similar research was also conducted by Sadakata, who studied the conversion of wood, lignin and holocellulose at a heating rate exceeding 1000°C/min. The maximum tar yield obtained by holocellulose was higher than that of other materials.

Devinder described the effect of steam content on tar formation during biomass gasification through a thermodynamic model. The simulation predicted that the more steam, the higher is the conversion efficiency of tar. Turn, Zainal and Lv also declared that the CO and H₂ fraction in product gases increased with steam/carbon ratio enhancement

Knight carried out biomass gasification under different pressures. Phenol was completely eliminated when the pressure was above 21.4 bar. However, the fraction of PAH increased with enhancing pressure though total tar decreased.

Besides affecting the fraction of tar during biomass gasification, operation parameters also influenced the tar properties. Paasen revealed that tar concentration decreased with temperature varying from 750 to 950 °C. Simultaneously, tar compositions shifted from alkyl-substituted poly-aromatic hydrocarbons(PAHs) to non-substituted PAHs.

Yu pyrolysed birch wood in a free-fall reactor to observe the temperature effect on the gasification process. He found that the amount of substituted 1- and 2-ring aromatics drastically went down with increasing temperature, and 3- and 4-ring aromatics yield was increased accordingly. Brage [reported an almost complete reduction of phenol content, 50% decrease in toluene content can be obtained when the temperature was raised from 700 to 900°C. However, benzene and naphthalene had inverse tendency, their contents varied from 14 to 24 mg/l and 2 to 8 mg/l, respectively.

Sousa performed tests to study how ER affected tar formation during wood gasification. The experimental results showed that the tar was a complex mixture of polycyclic aromatic compounds (benzene making 25% of the tars by mass, naphthalene 5.1%, indene 4.9%, acenaphthylene 1.7% and phenanthrene 1.4%), alkylated aromatic compounds (toluene 13.6%, styrene 5.3% and xylenes 5.2%) and phenolic compounds (phenol 15.1%, cresols 11.1%) at ER ¼ 0.2. When ER was increased to 0.3, the composition became less complex. The primary component was polycyclic aromatic compounds (benzene 42.9%, naphthalene 14.7%, indene 5.2%, acenaphthylene 4.4% and phenanthrene 3.9%), and the concentrations of alkylated aromatic compounds decreased remarkably. As

for phenolic compounds, cresols completely disappeared and only a small amount of phenol was detected. At ER ¼ 0.4, the tar was decomposed almost exclusively of benzene(60% of the tars by mass), naphthalene (17%) and a small amount of three and four ringed polycyclic aromatic hydrocarbons. Contrary to Sousa, Houben reported that increasing ER led to the formation of higher ring aromatic components.

3. THERMAL CRACKING

In thermal cracking method, the raw gases derived from gasification or pyrolysis were heated to a high temperature, where tar molecules can be cracked into lighter gases. Bridgewater viewed that tar could be reduced by thermal cracking in a fluidized bed gasifier. Meanwhile, the author also mentioned that biomass-derived tar was very refractory and hard to crack by thermal treatment alone. In order to effectively decompose the tar, the following ways were suggested: increasing residence time, such as using a fluidized bed reactor freeboard, but this method was only partially effective; Direct contacting with an independently heated hot surface, which required a significant energy supply and decreased the overall efficiency. At the same time, the method was also partly effective and depended on good mixing; Partial oxidation by adding air or oxygen could increase CO levels at the expense of conversion efficiency decrease and operation cost enhancement.

To achieve a sufficiently high tar cracking efficiency, Brandt claimed that the necessary temperature and residence time were 1250 °C and 0.5 s, respectively. Tar and soot content at 1200, 1250 and 1290 °C. According to the review of Beenackers and Manuatis, the preferable tar content in gases for engine application was below 50 mg/Nm³. Hence, 1250 °C was the limited temperature for tar decomposition.

Houben also carried out thermal tar cracking experiment at temperature range of 900–1150 °C and residence time between 1 and 12 s. In the experiment, naphthalene carried by nitrogen was used as model tar. The maximal tar reduction reached 98–99% at 900 °C with an excess air ratio of 0.5.

3.1. Catalyst cracking

Due to the advantages of converting tar into useful gases and adjusting the compositions of product gases, catalyst cracking has been of interest since the middle 1980s. The simplified mechanism for catalyst tar reforming can be described as follows. First, methane or other hydrocarbons are dissociatively adsorbed onto a metal site where metal-catalyzed dehydrogenation occurs. Water is also dissociatively adsorbed onto the ceramic support, hydroxylating the surface. At the appropriate temperature, the OH radicals migrate to the metal sites, leading to oxidation of the intermediate hydrocarbon fragments and surface carbon to CO+H₂. David summarized the criteria for catalyst as follows:

- E the catalysts must be effective in removing tar;
- F if the desired product was syngas, the catalysts must be capable of reforming methane;

- G The catalysts should provide a suitable syngas ratio for the intended process;
- H the catalysts should be resistant to deactivation as a result of carbon fouling and sintering;
- I the catalysts should be easily regenerated.
- J The catalysts should be strong; and
- K the catalysts should be inexpensive.

Moreover, David reviewed tar catalyst cracking and divided the catalysts into three groups: dolomite catalysts; alkali metal and other metal catalysts; nickel catalysts. After several years of developing, some new catalysts have been applied in gasification. Here, we group the catalysts into four groups and detailed description can be found in the following.

3.2. Ni-based catalyst

Ni-based catalysts are extensively applied in the petrochemical industry for naphtha and methane reforming. Meanwhile, a wide variety of Ni-based catalysts are commercially available. Especially, some studies showed that nickel based catalysts had the ability of reversing ammonia reaction, thus it is possible to reduce NO_x emission during biomass gasification.

Zhang investigated tar catalytic destruction in a tar conversion system consisting of a guard bed and catalytic reactor. Three Ni-based catalysts (ICI46-1, Z409 and RZ409) were proven to be effective in eliminating heavy tars (499% destruction efficiency). Hydrogen yield was also improved by 6–11 vol% (dry basis). The experimental results also demonstrated that space velocity had little effect on gas compositions, while increasing temperature boosted hydrogen yield and reduced light hydrocarbons (CH_4 and C_2H_4) formation, which suggested that tar decomposition was controlled by chemical kinetics.

Coll also studied the model compounds like benzene, toluene, naphthalene, anthracene, and pyrene were cracked using two commercial nickel catalysts: UCG90-C and ICI46-1 at 700–800 °C. The order of these model tars reactivity was: benzene > toluene > anthracene > pyrene > naphthalene. Toluene conversion rate ranged from 40% to 80% with the ICI46-1 catalyst, and 20% to 60% for the UCI G90-C catalyst.

Simell and co-workers reported the use of alumina and other catalysts with variable Ni content reformed toluene in various gas atmospheres at 900 °C and 0.5–20 MPa. The effects of sulfur poisoning on the activity of these catalysts for tar and ammonia decomposition had also been evaluated.

Nickel supported on silica was active for tar catalyst cracking at relatively low temperature (823 K) was described by Zhang. However, these catalysts only maintained their activities for a short time because of accumulating large amounts of carbon on their surfaces. Aznar and Baker also mentioned the phenomena in their experiments. In order to overcome the shortcoming of the commercial Ni-based catalyst, many Ni-based catalysts were developed.

Dou compared five catalysts on tar removal from fuel gases in a fixed-bed reactor. The Y-zeolite and Ni-Mo catalysts were found to be the most effective, such that 100% tar removal can be achieved at 550 °C. It was also observed that process variables like temperature and space velocity had very significant effect on tar removal. The visual observation demonstrated that only very small amount of coke appeared at the surface of catalyst even with 168 h operation. The result of Marino indicated that the addition of Ni into Cu/Ni/Kg– Al_2O_3 catalyst was favorable to gases yield increase and acetic acid production reduction during ethanol gasification.

Magnesium, lanthanum, and titanium oxide-doped nickel–chromium/alumina catalysts were prepared by Denis, and experiments were performed to assess the performance of these catalysts in steam reforming naphthalene. The experimental results revealed that the improved catalyst could promote conversion efficiency of naphthalene. After the structure analysis, it was found that MgO had a significant effect on the robustness of catalyst due to the formation of MgAl_2O_4 spinel phase.

Courson also developed a new Ni-based catalyst by impregnating nickel oxide on olivine and calcination at 900, 1100 and 1400 °C. X-ray diffraction, scanning electron microscopy and transmission electron microscopy coupled to energy dispersive X-ray spectroscopy analysis showed that there were interactions between the precursor and the support, which was consistent with the conclusion of Denis. After the characteristic studies, the catalyst performance tests indicated that the catalyst containing 2.8 wt% Ni calcined at 1100 °C was the optimum catalyst. Furthermore, no sintering and very little carbon deposition were observed on this catalytic surface.

Chen investigated CO_2 reforming methane over NiO/g– Al_2O_3 catalyst in a fixed/ fluidized bed. Francisco also compared the Ni catalyst supported on $\alpha\text{-Al}_2\text{O}_3$, ZrO_2 and $\alpha\text{-Al}_2\text{O}_3\text{-ZrO}_2$, and found Ni/ $\alpha\text{-Al}_2\text{O}_3\text{-ZrO}_2$ catalyst showed better performance. In the literature of Karen, he mentioned that the 1 wt%/0.5 wt% nickel/calcium catalyst co-precipitated inside porous filter discs can effectively remove tar (498%) even in the presence of 100 ppm H_2S .

3.3. Alkali metal catalysts

Besides Ni-based catalysts, many literatures proved that alkali metal catalysts were also effective in reforming tar. McKee successfully demonstrated that carbonates, oxides and hydroxides of alkali metals can effectively decompose tar during catalytic gasification.

Gong also studied waste paper gasification in carbon dioxide atmosphere with molten alkali metal carbonates including potassium, sodium, lithium carbonate or their intermixtures as catalyst. The molten catalysts were capable of facilitating a desired reaction ($\text{C} + \text{CO}_2 \rightarrow 2\text{CO}$), which was hardly feasible even at a high temperature of 973 K without catalysts. Further experimental results demonstrated that the intermixed carbonates exhibited stronger enhancement on catalytic ability than any carbonate salts in pure form. Waste paper gasification catalyzed by molten alkali carbonates was also investigated by Roman.

In the experiment of Demirba, three different biomass samples (cotton cocoon shell, tea factory waste and olive husk) were decomposed by direct and catalytic pyrolysis process to obtain hydrogen rich gaseous products at 775, 925, 975 and 1025 K. In the catalytic pyrolysis process, the yield of hydrogen rich gases was increased in the case of using $ZnCl_2$ catalyst though the yield of charcoal and liquid products were also increased. While the effect of K_2CO_3 and Na_2CO_3 on pyrolysis products depended on the biomass species. It was found that the Na_2CO_3 was better than K_2CO_3 for the cotton cocoon shell and tea factory waste pyrolysis. Nevertheless, in the case of olive husk pyrolysis, the conclusion is opposite, and K_2CO_3 was more effective than Na_2CO_3 . At the same time, the effect of the amount of Na_2CO_3 and K_2CO_3 on the pyrolysis products was irregular.

Pant and Kumar also pyrolysed n-heptane over different calcium aluminates and potassium impregnated calcium aluminate in a fixed bed reactor. Compared to the unpromoted catalysts, K_2CO_3 impregnated catalyst significantly suppressed the coke deposited on the catalyst surface, but only had marginal effect on the product selectiveness. Brown also found alkali metal salts, especially those containing potassium, were excellent promoters for gasification reactions. On the contrary to the conclusion of Brown, a gravimetric study of the alkali metal hydridotetracarbonyl-ferrates catalytic activity at 800 °C revealed the following sequence with respect to the cation activity: $Na4Li4 K4Rb4Cs$.

3.4. Dolomite catalysts

Dolomite is a calcium magnesium ore with general chemical formula $CaMg(CO_3)_2$, and is generally used as raw material in the manufacture of magnesium. In recent years, it has been discovered that calcined dolomite is also a highly efficient catalyst for removing tar from the product gases of gasifier.

Simell compared a commercially available metal based catalyst ($NiMo/g-Al_2O_3$) with non-metallic mineral catalysts during the catalytic pyrolysis of toluene. The non-metallic mineral catalysts included Norwegian dolomitic magnesium oxide [MgO], Swedish low surface quicklime [CaO], and calcined dolomite [$CaMg(O)_2$]. Among these catalysts, the catalytic effect followed the sequence: $CaO4CaMg(O)_24MgO4NiMo/g-Al_2O_3$.

Rui and Rapagn claimed that the presence of dolomite in the fluidized bed had the benefit of decreasing tar content and rising gases yield. However, dolomite could not affect gaseous hydrocarbons concentrations. It was reported that an amount of 20–30 wt% dolomite (rest being silica sand) in the gasifier reduced tar content to about $1 g/m^3$ at an ER of 0.3. The authors also studied the influence of several operating parameters combined with using in-bed dolomite.

Devi reported that untreated olivine could convert only 46% tar in the hot gasification gases, which could not be considered as a significant reduction. While catalyst was pre-treated olivine, the conversion of naphthalene, considered as a model biomass tar compound, was as high as 80%. The pretreatment was only heating the olivine catalyst at 900 °C in the presence of air. It was expected that the calcination could activate olivine.

Karlsson successfully demonstrated biomass integrated gasification with combined cycle (IGCC) process with dolomite as bed material. Only about $1-2 g/m^3$ of light tars (excluding benzene) and $100-300 mg/m^3$ of heavy tars were detected in the product gases.

Srinakruang and Wang developed a new catalyst (Ni supported by dolomite), which could maintain high activity and stability for a long contact time. Moreover, carbon deposition at the Ni/dolomite catalysts surface was negligible. The authors also claimed that the calcination temperature significantly influenced the property and activity of the Ni/dolomite catalyst since nickel oxide had strong interaction with the dolomite surface.

Although the dolomite can effectively remove tar in some cases, there are still many problems during biomass gasification. Zhang reviewed the shortcomings of dolomite as the following: The conversion rate of tar catalyzed by dolomite was difficult to reach or exceed 90–95%; Although dolomite could reduce the tar in syngas and change the distribution of tar compositions, it was difficult to convert the heavy tars by dolomite; The dolomite would be inactive since the particle was easily broken during gasification; The melting point of dolomite was low and the catalyst would be inactive resulting from the melting of dolomite.

3.5. Novel metal catalysts

Ni-based catalysts and dolomite were deactivated significantly by carbon deposition and alkali metal was easily sintered. Novel metals had been widely used as catalyst for NO_x and SO_2 since 1980s. Some researchers found that the novel metal catalysts were able to overcome the shortcomings of conventional catalyst, and keep high efficiency on converting tar. Tomishige compared the tar conversion rates over $M/CeO_2/SiO_2$ ($M = \frac{1}{4} Rh, Pd, Pt, Ru, Ni$) catalyst during cellulose gasification. The order of catalyst activity in the cedar wood gasification at 823 K was the following: $Rh4Pd4Pt4Ni = \frac{1}{4} Ru$. The tar conversion rate was about 88% in the case of $Rh/CeO_2/SiO_2$ catalyst at 823 K, which jumped to the 97% at 873 K. Since the amount of char on $Rh/CeO_2/SiO_2$ catalyst surface was very small at low temperature, no deactivation was observed during the operation period. In addition, $Rh/CeO_2/SiO_2$ exhibited high and stable activity even under the presence of high concentration of H_2S (280 ppm).

Asadullah and coworker also studied the performance of various kinds of $Rh/CeO_2/M$ -type ($M = \frac{1}{4} SiO_2, Al_2O_3, ZrO_2$) catalysts for cellulose gasification in a continuous-feeding fluidized-bed reactor. Among the catalysts, $Rh/CeO_2/SiO_2$ exhibited the best performance with respect to generating syngas or hydrogen. Moreover, Pt, Ru, Pd, and Ni doped on CeO_2 , and supported by $SiO_2, Al_2O_3, TiO_2, MgO$, and ZrO_2 were also tested and the results also proved that Rh/CeO_2 was the best catalyst. However, in the continuous-feeding system, it was found that the Rh/CeO_2 catalyst suddenly deactivated due to a decrease in surface area from 60 to $13 m^2/g$. After further study, the authors found that the loading of CeO_2 on the high-surface-area SiO_2 could inhibit the aggregation of CeO_2 and maintain the catalytic activity. Among various loadings, 35% wt CeO_2 on SiO_2 was the most suitable support for Rh in terms of the tar conversion, gas yield, and fast char conversion.

The catalytic performances of Co catalysts for the steam reforming of naphthalene were reported by Furusawa. The characterizations analysis (TPR, XRD, CO adsorption, and CO-TPD) of catalysts showed that the large-sized Co metal particles were formed over the precalcined catalysts.

Hao investigated Ru/C, Pd/C, CeO₂ particles, nano-CeO₂ and nano-(CeZr)_xO₂ catalytic cracking tar during cellulose and sawdust gasification. The experimental results demonstrated that the catalyst activities followed the order: Ru/C4Pd/C4nano-(CeZr)_xO₂4nano-CeO₂ 4CeO₂. Rh supported on CeO₂, ZrO₂ and SiO₂ single metal oxides and various mixed metal oxides such as CeO₂/SiO₂, ZrO₂/SiO₂ and CeO₂/ZrO₂ were compared by Polychronopoulos, and found that 1.5 wt% Rh/CeO₂/ZrO₂ catalyst, the support of which was prepared by the sol-gel method, exhibited better performance than other catalysts.

Sutton also studied the activity of the 3:17 Ni/Al co-precipitated catalyst with 1 wt% Ru/Al₂O₃ and 1 wt% Pt/ZrO₂ for dry reforming CH₄ and C₃H₈ at 450–800 °C. Rapagna developed a catalyst with a chemical formula of LaNi_{0.3}Fe_{0.7}O₃, which was prepared by means of a sol-gel related process, where La, Ni, and Fe nitrate salts were dissolved separately in hot propionic acid. The catalyst displayed high CH₄ reforming activity at 800°C. Garcia also reported that cobalt-promoted and chromium-promoted nickel catalysts supported on a MgO-La₂O₃-Al₂O₃ performed the best in terms of H₂ yield and lifetime.

4. CONCLUSIONS

This study has collected the information on the reactivity, tar formation and the technology of the tar during pyrolysis/Gasification process from the published journals.

Although the primary use of mechanism methods is to capture the fly ash or particles from the product gases, the effect of gas removal is very good about 40-99% of tar can be reduced by different mechanism methods.

The Gasification/Pyrolysis not only produces only useful fuel gases, but also same products like fly ash, NO_x, SO₂ and tar. The different type of cracking methods such as thermal cracking where in the raw gases derived from the gasification where heated to high temperature where the tar molecules cracked into the lighter gases, catalyst cracking, Ni based catalyst, Alkali metal catalyst, Dolomite catalyst and Novel metal catalyst method of cracking were studied in the above work.

REFERENCE

- [1] Shogun Li, Xu S, Liu S, Yang C, Lu Q. Fast pyrolysis of biomass in free-fall reactor for hydrogen-rich gas. *Fuel Process Technol* 2004; 85:1201–11.
- [2] Hasler. Evaluation of gas cleaning technologies for small scale biomass gasifiers. Zurich: Swiss Federal Office of Energy and Swiss Federal Office for Education and Science, 1997.
- [3] Li XT, Grace JR, Lim CJ, Watkinson AP, Chen HP, Kim JR. Biomass gasification in a circulating fluidized bed. *Biomass Bioenergy* 2004; 26:171–93.
- [4] Asadullah M, Miyazawa T, Kunimori K. Catalyst development for the gasification of biomass in the dual-bed gasifier. *Appl Catal A: Gen* 2003;255:169–80.
- [5] Lopamudra D, Ptasiniski KJ, Janssen FJJG. A review of the primary measures for tar elimination in biomass gasification processes. *Biomass Bioenergy* 2003;24:125–40
- [6] Demirbas A. Potential applications of renewable energy sources, biomass combustion problems in boiler power systems and combustion related environmental issues. *Progr Energy Combust Sci* 2005;31:171–92.
- [7] Kosstrin H. Direct formation of pyrolysis oil from biomass. In: Proceedings specialists workshop on fast pyrolysis of biomass, 1980.
- [8] Sadakata M, Takahashi K, Saito M, Sakai T. Production of fuel gas and char from wood, lignin and holocellulose by carbonisation. *Fuel* 1987;66:1667–71.
- [9] Singh D, Hernandez-Pacheco E, Hutton PN, Patel N. Carbon deposition in an SOFC fueled by tar-laden biomass gas: a thermodynamic analysis. *J Power Sourc* 2004;142:194–9.
- [10] Turn S, Kinoshita C, Zhang Z, Ishimura D, Zhou J. An experimental investigation of hydrogen production from biomass gasification. *Int J Hydrogen Energy* 1998;23:641–8.
- [11] Knight RA. Experience with raw gas analysis from pressurized gasification of biomass. *Biomass Bioenergy* 2000;18:67–77.
- [12] Yu Q, Brage C, Chen G. Temperature impact on the formation of tar from biomass pyrolysis in a free-fall reactor. *J Analyt Appl Pyrol* 1997;40–41:481–9.
- [13] Hasler P, Nussbaumer T. Gas cleaning for IC engine applications from fixed bed biomass gasification. *Biomass Bioenergy* 1999;16:385–95.
- [14] Fagbemi L, Khezami L, Capart R. Pyrolysis products from different biomasses application to the thermal cracking of tar. *Appl Energy* 2001;69:293–306.
- [15] Claes B. Characteristics of evolution of tar from wood pyrolysis in a fixed-bed reactor. *Fuel* 1996;75: 213–9.
- [16] Anna P, Sylwester K, Wlodzimierz B. Effect of operating conditions on tar and gas composition in high temperature air/steam gasification (HTAG) of plastic containing waste. *Fuel Process Technol* 2006;87: 223–33.
- [17] Morf P. Mechanisms and kinetics of homogeneous secondary reactions of tar from continuous pyrolysis of wood chips. *Fuel* 2002;81:843–53.
- [18] Sousa LCR. Gasification of wood, urban wastewood (Altholz) and other wastes in a fluidised bed reactor. Technische Wissenschaften ETH Zu'rich; 2001.
- [19] Houben MP. Analysis of tar removal in a partial oxidation burner. The dissertation of Eindhoven University, 2004.
- [20] Sutton D, Kelleher B, Ross JRH. Review of literature on catalysts for biomass gasification. *Fuel Process Technol* 2001;73:155–73.
- [21] Bentzen JD. Low tar and high efficient gasification concept. In: Proceedings of the conference ECOS, 2000.[46] Colomba DB. Modeling intra- and extra-

- particle processes of wood fast pyrolysis. *AIChE J* 2002;48: 2386–97.
- [22] Brandt P, Ulrik Henriksen. Decomposition of tar in gas from updraft gasifier by thermal cracking. In: *Proceedings of the first world conference on biomass for energy and industry*; 2000.
- [23] Beenackers, Maniatis K. Gasification technologies for heat and power from biomass. In: *Proceedings of biomass for energy and environment ninth European bioenergy*, 1996.
- [24] Ding Xiaohui. Catalytic Decomposition of ammonia in producer gas. The dissertation of Zheng zhou University(China), 2003.
- [25] Dayton D. A review of the literature on catalytic biomass tar destruction. USA: National Renewable Energy Laboratory; 2002.
- [26] Hepola J, McCarty J, Krishnan G, Wong V. Elucidation of behavior of sulfur on nickel-based hot gas cleaning catalysts. *Appl Catal B: Environ* 1999;20:191203.
- [27] Ekstrom C, Lindman N, Petersson R. *Fundamentals of thermochemical biomass conversion*. London and New York: Elsevier Applied Science; 1988.
- [28] Mudge LK, Baker E, Brown MD. *Research in thermochemical biomass conversion*. London and New York: Elsevier Applied Science; 1988.
- [29] Bridgwater P, Anthony V. *Thermochemical processing of biomass*. Butterworth; 1984.
- [30] Strom E, Linanki L, Sjostrom K. *Biomass conversion*. London: Elsevier Applied Science; 1985.
- [31] Aznar MP, Delgado J. *Biomass for energy and industry*. Amsterdam: Elsevier; 1992.
- [32] Zhang R, Brown RC, Suby A, Cummer K. Catalytic destruction of tar in biomass derived producer gas. *Energy Convers Manage* 2004;45:995–1014.
- [33] Furusawa T, Tsutsumi A. Comparison of Co/MgO and Ni/MgO catalysts for the steam reforming of naphthalene as a model compound of tar derived from biomass gasification. *Appl Catal A: Gen* 2005;278: 207–12.
- [34] Filippis PD, Borgianni C, Paolucci M, Pochetti F. Gasification process of Cuban bagasse in a two-stage reactor. *Biomass Bioenergy* 2004;27:247–52.
- [35] Dou B, Gao J, Sha X, Baek SW. Catalytic cracking of tar component from high-temperature fuel gas. *Appl Therm Eng* 2003;23:2229–39.
- [36] Coll R, Salvado J, Farriol X, Montane D. Steam reforming model compounds of biomass gasification tars: conversion at different operating conditions and tendency towards coke formation. *Fuel Process Technol* 2001;74:19–31.
- [37] Lappas AA, Samolada MC, Iatridis DK, Voutetakis SS. Biomass pyrolysis in a circulating fluid bed reactor for the production of fuels and chemicals. *Fuel* 2002;81:2087–95.
- [38] Engelen K, Zhang Y, Draelants DJ, Baron GV. A novel catalytic filter for tar removal from biomass gasification gas: improvement of the catalytic activity in presence of H₂S. *Chem Eng Sci* 2003;58: 665–70.
- [39] Taralas G, Kontominas MG. Kinetic modeling of VOC catalytic steam pyrolysis for tar abatement phenomena in gasification/pyrolysis technologies. *Fuel* 2004; 83:1235–45.
- [40] Marin`o F, Cerrella E. Hydrogen from steam reforming of ethanol. Characterization and performance of copper–nickel supported catalysts. *Int J Hydrogen Energy* 1998;23:1095–102.
- [41] Simell P, Kurkela E. Tar removal from gasification gas in biomass gasification and pyrolysis. CPL Press; 1997.
- [42] Simell P, Kurkela E, Sta`hlberg P, Hepola J. Catalytic hot gas cleaning of gasification gas. *Catal Today* 1996;27:55–62.
- [43] Simell P, Kurkela E, Sta`hlberg P, Hepola J. Development of catalytic gas cleaning in biomass gasification. *VTT symp* 1996;164:133–40.
- [44] Simell P, Kurkela E, Sta`hlberg P, Hepola J. Provisional protocol for the sampling and analysis of tar and particulates in the gas from large-scale biomass gasifiers. *Biomass Bioenergy* 2000;18:19–38.
- [45] Zhang T, Amiridis MD. Hydrogen production via the direct cracking of methane over silica-supported nickel catalysts. *Appl Catal A: Gen* 1998;167:161–72.
- [46] Marin`o F, Boveri M. Hydrogen production via catalytic gasification of ethanol. A mechanism proposal over copper–nickel catalysts. *Int J Hydrogen Energy* 2004;29:67–78.
- [47] Bangala DN. Steam reforming of naphthalene on Ni–Cr/Al₂O₃ catalysts doped with MgO, TiO₂, and La₂O₃. *AIChE* 1998;44:927–36.
- [48] Courson C, Makaga E, Petit C, Kiennemann. Development of Ni catalysts for gas production from biomass gasification. Reactivity in steam- and dry-reforming. *Catal Today* 2000;63:427–37.
- [49] Courson C, Udron L, Petit C, Kiennemann A. Grafted NiO on natural olivine for dry reforming of methane. *Sci Technol Adv Mater* 2002;3:271–82.
- [50] Courson C, Udron L, Swierczynski D, Petit C, Kiennemann A. Hydrogen production from biomass gasification on nickel catalysts: tests for dry reforming of methane. *Catal Today* 2003;76:75–86.
- [51] Chen X, Honda K, Zhang ZG. CO₂, CH₄ reforming over NiO/g-Al₂O₃ in fixed/fluidized-bed multi-switching mode. *Appl Catal A: Gen* 2005;279:263–71.
- [52] ompeo F, Nichio NN, Ferretti OA, Resasco D. Study of Ni catalysts on different supports to obtain synthesis gas. *Int J Hydrogen Energy* 2005 [in press].
- [53] Engelen K, Zhang Y, Draelants DJ, Baron GV. Novel catalytic filter for tar removal from biomass gasification gas: Improvement of the catalytic activity in presence of H₂S. *Chem Eng Sci* 2003;58:665–70.
- [54] Iwaki H, Shufeng Ye. Wastepaper gasification with CO₂ or steam using catalysts of molten carbonates. *Appl Catal A: Gen* 2004;270:237–43.
- [55] Jin G, Iwaki H, Arai N, Kitagawa K. Study on the gasification of wastepaper/carbon dioxide catalyzed by molten carbonate salts. *Energy* 2005;30:1192–203.
- [56] McKee DW. Mechanisms of the alkali metal catalysed gasification of carbon. *Fuel* 1983;62:170–5.

- [57] Roman A, Michael E. Solar gasification of biomass: a molten salt pyrolysis study. *J Sol Energ Eng* 2004; 126:850–7.
- [58] Demirba A. Gaseous products from biomass by pyrolysis and gasification: effects of catalyst on hydrogen yield. *Energ Convers Manage* 2002;43:897–909.
- [59] Pant KK. Catalytic pyrolysis of n-heptane on unpromoted and potassium promoted calcium aluminates. *Chem Eng J* 2002;87:219–25.
- [60] Kumar VA, Anil Kumar V, Pant KK. Potassium-containing calcium aluminate catalysts for pyrolysis of n-heptane. *Appl Catal A: Gen* 1997;162:193–200.
- [61] Andre RN, Pinto F, Franco C, Dias M, et al. Fluidised bed co-gasification of coal and olive oil industry wastes. *Fuel* 2005;84:1635–44.
- [62] RapagnVa S, Jand N, Foscolo PU. Catalytic gasification of biomass to produce hydrogen rich gas. *Int J Hydrogen Energ* 1998;23:551–7.
- [63] Gil J, Caballero MA. Biomass gasification with air in fluidized bed: effect of in-bed use of dolomite under different operation conditions. *Ind Eng Chem Res* 1999;138:4226–35.
- [64] Devi L. Catalytic removal of biomass tar: Olivin as prospective in bed catalyst for fluidized bed biomass gasifiers. The dissertation of Technische Universiteit Eindhoven, 2005.
- [65] Devi L, Ptasinski KJ, Janssen FJJG, Van Paasen SVB. Catalytic decomposition of biomass tars: use of dolomite and untreated olivine. *Renew Energ* 2005;30:565–87.
- [66] Devi L, Ptasinski KJ, Janssen FJJG. Pretreated olivine as tar removal catalyst for biomass gasifiers: investigation using naphthalene as model biomass tar. *Fuel Process Technol* 2005;86:707–30.
- [67] Karlsson G, Ekstr. The development of a biomass IGCC process for power and heat production. In: Proceedings of the eighth European conference on biomass for energy, environment, agriculture and industry, 1994.
- [68] Srinakruang J, Sato K, Vitidsant T, Fujimoto K. A highly efficient catalyst for tar gasification with steam. *Catal Commun* 2005;6:437–40.
- [69] Wang TJ, Chang J, Wu CZ, Fu Y, Chen Y. The steam reforming of naphthalene over a nickel–dolomite cracking catalyst. *Biomass Bioenerg* 2005;28:508–14.
- [70] Zhang Xiaodong. The mechanism of tar cracking by catalyst and the gasification of biomass. The dissertation of Zhejiang University (China), 2003.
- [71] Heejoon Kim, Mizuno A. Development of a new desulfurization process by a non thermal plasma hybrid reactor. *Energ Fuel* 2002;6:803–8.
- [72] Yanli W, Liu Z, Zhan L, Huang Z, Liu Q, Ma J. Performance of an activated carbon honeycomb supported V₂O₅ catalyst in simultaneous SO₂ and NO removal. *Chem Eng Sci* 2004;59:5283–90.
- [73] Tian LQ, Daiqi Ye. Catalytic performance of a novel ceramic-supported vanadium oxide catalyst for NO reduction with NH₃. *Huan Jing Ke Xue* 2004;25:7–13.
- [74] Tomishige K, Asadullah M, Kunimori K. Syngas production by biomass gasification using Rh/CeO₂/SiO₂ catalysts and fluidized bed reactor. *Catal Today* 2004;89:389–403.
- [75] Haga F, Nakajima T, Miya H, Mishima S. Catalytic properties of supported cobalt catalysts for steam reforming of ethanol. *Catal Lett* 1997;48:223–7.
- [76] Hao X, Guo L, Zhang X, Guan Y. Hydrogen production from catalytic gasification of cellulose in supercritical water. *Chem Eng Sci* 2005;60:1–9.
- [77] Polychronopoulou K, Costa CN, Efstathiou AM. The steam reforming of phenol reaction over supported-Rh catalysts. *Appl Catal A: Gen* 2004;272:37–52.
- [78] Sutton D, Parle SM, Ross JRH. The CO₂ reforming of the hydrocarbons present in a model gas stream over selected catalysts. *Fuel Process Technol* 2002;75:45–53.
- [79] Rapagna S, Provendier H, Petit C, Kiennemann A, Foscolo PU. Development of catalysts suitable for hydrogen or syngas production from biomass gasification. *Biomass Bioenerg* 2002;22:377–88.
- [80] C.-Z.Li and P.F.Nelson: Fate of aromatic ring systems during thermal cracking of tars in a fluidized-bed reactor. *Energy Fuels* 10 (5) 1083-1090 (1996).
- [81] T.Milne, N.Abatzoglou and R.J.Evans: Biomass gasifier "tars": their nature, formation and conversion, Golden, CO (USA), NREL, NREL/TP-570-25357, 68 p. (1998).
- [82] CRE Group: Identification and processing of biomass gasification tars, Cheltenham (UK), CRE Group Ltd, ETSU-B-T1-00418/REP, 26 p. (1997).
- [83] R.Cyprès and C.Lejeune: Craque thermique de m-crésol, du bènezene, du toluène et du phénol entre 650 et 850°C. *Ann. Mines Belgique* 7-8 1091-1109 (1965).
- [84] A.Jess: Mechanisms and kinetics of thermal reactions of aromatic hydrocarbons from pyrolysis of solid fuels. *Fuel* 75 (12) 1441-1448 (1996).
- [85] F.Kopinke, G.Zimmermann, G.C.Reyniers and G.F.Froment: Relative rates of coke formation from hydrocarbons in steam cracking of naphtha: 3. Aromatic hydrocarbons. *Ind. Eng. Chem. Res.* 32 (11) 2620-2625 (1993).
- [86] P.A.Tesner, I.S.Rafal'kes and O.B.Zhedeneva: Influence of hydrogen on the kinetics of the formation of pyrocarbon in the thermal decomposition of aromatic