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REVIEWS

Review of Catalysts for Tar Elimination in Biomass Gasification Processes

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A project is carried out to develop a process for tar elimination downstream of a gasifier making use of cheap and active materials as catalysts. In the first stage of the project, screening of catalysts was carried out in a fixed-bed tubular reactor. The results of the fixed-bed experiments will be used in the design of the process. This paper presents a review of the various types of catalysts that have been used in several research works to reduce the tars in the producer gas derived from the biomass gasification process. The catalysts are divided into two classes according to their production method: minerals and synthetic catalysts. A summary of the review and recommendations for good catalyst candidates and future work are also provided.

1. Introduction

The contribution of biomass to the world's energy supply is presently estimated to be around 10−14%.[1] The European Union aims to achieve 12% renewable energies and 23% electricity from renewable energies by 2010.[2] Biomass can be defined as any organic material of plant origin. It is expected that biomass gasification technologies will be an important part of the attempt to meet the goals of expanding the use of biomass. Gasification involves the partial combustion of biomass to produce gaseous fuels (fuel gases or synthesis gases) by heating in a gasification medium such as air, oxygen, or steam. These gaseous products have many applications such as[3,4] generation of heat or electricity, synthesis of liquid transportation fuels, production of hydrogen fuel, synthesis of chemicals, and manufacturing of fuel cells. On the other hand, these gaseous products need to be cleaned from different types of impurities such as[5] (a) solid impurities (dust); (b) inorganic impurities such as nitrogen compounds (NH_3 and HCN), sulfur compounds (H_2S), ash, and metal compounds; and (c) organic impurities (tars). Table 1 shows the gas quality requirements for power generation.[6]

One of the main technical barriers in biomass gasification development is the presence of organic impurities (tars) in the fuel gas. These tars can cause several problems, such as[7] cracking in the pores of filters, forming coke and plugging them, and condensing in the cold spots and plugging them, resulting in serious operational interruptions. Moreover, these tars are dangerous because of their carcinogenic character, and

Table 1. Gas Quality Requirements for Power Generation[6]

		IC engine	gas turbine
particle concentration	mg/Nm^3	<50	<30
particle size	μm	<10	<5
tar	mg/Nm^3	<100	n.i.^{a}
alkali metals	mg/Nm^3	n.i.^{a}	0.24

^{a} n.i. = not indicated. Reprinted from *Biomass and Bioenergy*, *16*, Hasler, P. and Nussbaumer, Gas Cleaning for IC Engine Applications from Fixed Bed Biomass Gasification. pp 385−395, copyright (2004), with permission from Elsevier.

they contain significant amounts of energy that can be transferred to the fuel gas as H_2, CO, CH_4, etc. In addition, high concentrations of tars can damage or lead to unacceptable levels of maintenance for engines and turbines. Tars are defined as a generic (unspecific) term comprising all organic compounds present in the producer gas excluding gaseous hydrocarbons (C1−C6) and benzene.[8] Figure 1 shows the typical composition of biomass tars.[9] However, this composition depends on the type of fuel and the gasification process.

In general, tars can be removed by physical, noncatalytic (e.g., thermal cracking), and catalytic tar elimination processes. Catalytic tar conversion is a technically and economically interesting approach for gas cleaning. Such an approach is intuitively interesting because it has the potential to increase conversion efficiencies while simultaneously eliminating the need for the collection and disposal of tars. The catalytic conversion of tars is commonly known as hot gas cleaning. The research on catalytic tar conversion involves two methods:[4,10] (a) One approach involves incorporating or mixing catalyst with the feed biomass to achieve so-called catalytic gasification or pyrolysis (also called in situ). This method is a one of the primary methods used for tar reduction, where the tar is removed in the gasifier itself. (b) In the second approach, the gasifier producer gas is treated downstream of the gasifier in a

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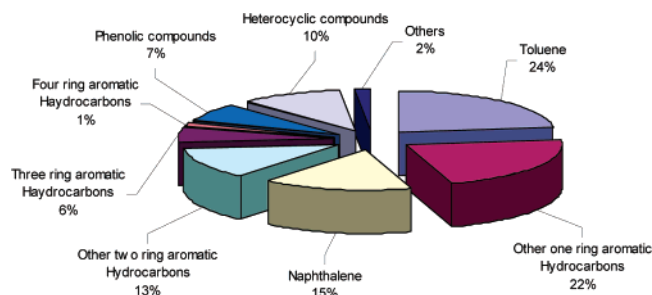† University of Twente.
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Figure 1. Typical composition of biomass tars (wt %)[9] (modified). Reprinted from *Fuel Processing Technol.*, *74*, Coll, R.; Salvadó, J.; Farriol, X.; Montané, D. Steam Reforming Model Compounds of Biomass Gasification Tars: Conversion at Different Operating Conditions and Tendency towards Coke Formation. pp 19−31, copyright (2004), with permission from Elsevier.
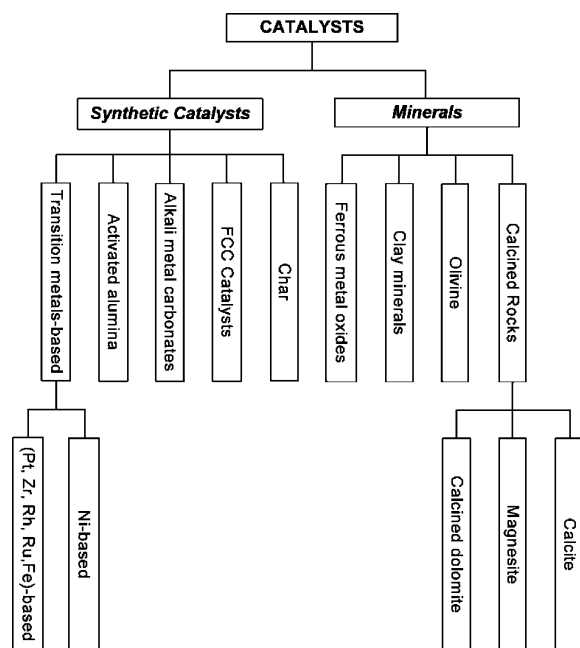

Figure 2. Classification and types of catalysts used for tar elimination.

secondary reactor. This method is a one of the secondary methods used for tar reduction, where the tar is removed outside the gasifier.

Bridgwater et al.[11] reviewed three groups of catalysts for biomass gasification: dolomites; fluid catalytic cracking catalysts; and nickel and other precious metals such as platinum, palladium, and rhodium. Later, Sutton et al.[12] reviewed another three groups of catalysts for biomass gasification. These catalysts were dolomites, alkali metals, and nickel.

This paper presents a review of nine groups of catalysts that have been used to reduce the tars in the producer gas obtained from the gasification process. The catalysts are reviewed according to the following points: (a) chemical composition, (b) factors of catalytic activity for tar elimination, (c) factors of catalytic deactivation, (e) advantages and disadvantages, and (e) some important results of research on the catalyst. The catalysts are divided into two classes on the basis of their production method: minerals and synthetic catalysts. Figure 2 shows the different reviewed catalysts that belong to these classes

2. Catalysts

Tar elimination reactions are known to be kinetically limited. Therefore, the reaction rates can be increased by increasing the temperature and/or using a catalyst. However, catalysts can only increase the rate of a reaction that is thermodynamically feasible. Several reactions can occur in a secondary catalytic reactor downstream of the gasifier. The most important reactions are listed in Table 2.

This section discusses the two classes of catalysts used in tar reduction for biomass gasification in the order presented in Figure 2.

2.1. Minerals. Minerals are naturally occurring, homogeneous solids with a definite, but generally not fixed, chemical composition and an ordered atomic arrangement.[16] The catalysts belonging to this class are are available in nature and can be used directly or with some physical treatment (such as heating) but without chemical treatment. In general, it can be noted that mineral catalysts are relatively cheap compared to synthetic catalysts.

2.1.1. Calcined Rocks. These catalysts contain alkaline earth metal oxides (CaO and/or MgO). Alkaline earth metals include any of the divalent electropositive metals beryllium, magnesium, calcium, strontium, barium, and radium, belonging to group 2A of the periodic table. Calcined rocks include calcites, magnesites, and calcined dolomites. Simell et al.[17] classified such catalysts according to the CaO/MgO ratio as shown Table 3. These catalysts have other names such as alkaline earth oxides, stones, minerals, and naturally occurring catalysts. The uncalcined forms of these materials are called limestone ($CaCO_3$), magnesium carbonate ($MgCO_3$), and dolomite ($CaCO_3 \cdot MgCO_3$), respectively.

Table 4 lists some examples of the chemical compositions of these materials.[18] These materials show catalytic activity for tar elimination when calcined. Calcination occurs because of the loss of bound carbon dioxide when the material is heated. The reactions involved in tar elimination over these materials are not well known. However, these reactions include at least reactions 1−4 listed in Table 2.

Simell et al.[16] related the catalytic activity for tar elimination of the calcined rocks to several factors such as a large pore size and surface area of the corresponding calcinates and a relatively high alkaline (K, Na) content. Alkaline metals could act as promoters present in commercial steam-reforming catalysts by enhancing the gasification reaction of carbon intermediates deposited on the catalyst surface.[17] The activity of these rocks can be improved by increasing the Ca/Mg ratio, decreasing the grain size, and increasing the active metal content such as iron.[17] The factors that cause catalytic deactivation of the calcined rocks are related to coke formation and CO_2 partial pressure. Coke causes deactivation of the calcined rocks by covering their active sites and blocking their pores.[18] Coke is produced by the catalytic reactions involving tar side reactions that occur on the catalyst surface. The CO_2 partial pressure causes deactivation when it is higher than the equilibrium decomposition pressure of the carbonated form of the material under the same conditions.[19]

The advantages of these materials are that they are inexpensive and abundant. Dolomites can provide relatively high tar conversion (up to 95%). They are often used as guard beds to protect the expensive and sensi-

Table 2. Important Reactions in a Secondary Catalytic Reactor Downstream of the Gasifier

ref(s)	reaction type[b]	reaction	
13, 14	steam reforming	$C_nH_m + nH_2O \rightleftharpoons nCO + \left(n + \frac{m}{2}\right)H_2$	(1)
13, 14	dry reforming	$C_nH_m + nCO_2 \rightleftharpoons 2nCO + \left(\frac{m}{2}\right)H_2$	(2)
15[b]	thermal cracking	$C_nH_m \rightarrow C^* + C_xH_y + gas$	(3)
13, 14	hydrocracking or hydroreforming of tars	$C_nH_m + H_2 \rightleftharpoons CO + H_2 + CH_4 + \cdots + coke$	(4)
15	water−gas shift reaction	$CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$	(5)

[a] C_nH_m hydrocarbons represent tars. C_xH_y hydrocarbons represent lighter tars. [b] Modified.

Table 3. Classification of Calcined Rocks Based on Ca/MgO Ratio as Presented by Simell et al.[17]

type	CaO/MgO ratio
limestone	>50
dolomitic limestone	4−50
calcitic dolomite	1.5−4
dolomite	1.5

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Table 4. Chemical Composition (wt %) Examples of Limestone, Magnesium Carbonate, and Dolomite[18]

component	calcite morata[a]	magnesite navarra[b]	dolomite norte[c]
CaO	53.0	0.7	30.9
MgO	0.6	47.1	20.9
CO_2	41.9	52.0	45.4
SiO_2	2.7		1.7
Fe_2O_3	0.8		0.5
Al_2O_3	1.0		0.6

[a] Zaragoza, Spain. [b] Navarra, Spain. [c] Bueras, Cantabria, Spain.

Table 5. Chemical Composition of a Selected Commercial Olivine[23]

component	wt %
MgO	48.5−50.0
CaO	0.05−0.10
SiO_2	41.5−42.5
Fe_2O_3	6.8−7.3
Al_2O_3	0.4−0.5
NiO	0.3−0.35
MnO	0.05−0.10
Cr_2O_3	0.2−0.3

tive metal catalysts from deactivation caused by tars or other impurities such H_2S. Dolomites are considered the most popular cheap catalysts for tar elimination. The main problem with these materials is their fragility. They are very soft and quickly eroded in fluidized beds with high turbulence.[18]

Delgado et al.[18] found that the reactivity of these catalysts was in the order calcined dolomite > calcite > magnesite. Dolomites can be of different types depending on their origin, and consequently, they differ in composition. Simell et al.[17] found that kalkkimaa dolomite (0.8 wt % Fe) and Ankerite dolomite (4.6 wt % Fe) are highly active dolomites. Orio et al.[13] tested the activities of different dolomites and found the following order: Chilches dolomite > Norte dolomite > Malaga dolomite. They related the difference in activity to the iron oxide (Fe_2O_3) content, being 0.74−0.84, 0.12, and 0.01, respectively. In situ use of calcined rocks is employed by Walwander et al.[20] in the U.S., Corella et al. in Spain, and Kurkela et al. in Finland. The Finnish companies Tampella Power Oy, Carbona Inc., and VTT also prefer in situ use.[18] The University of Zaragoza (Zaragoza, Spain) found that the in situ use of dolomite is somewhat less effective than its use downstream from the gasifier.[21] Tar contents in the raw flue gas below 1 g/Nm³ are obtained using a bed with a content of between 15 and 30 wt % of dolomite, with the rest being silica sand.[10] Gil et al.[10] reported that the in situ use of dolomite generates higher carryover of solids from the gasifier bed with correspondingly higher particulates contents in the raw producer gas. The in situ use of dolomite has the lowest cost and the lowest tar reduction. A secondary bed of dolomite is preferred by the

Swedish company TPS AB. TPS has demonstrated the success of tar cracking over dolomite in a secondary reactor that is close-coupled with their circulating fluidized-bed gasifier. This method seems to be more successful than the in situ addition of dolomite, giving tar reductions of up to 95%. With this method (use of a secondary bed of dolomite downstream from the gasifier), Corella and co-workers obtained a reduction of the tar content in the fuel gas to a level of about 1.2 g/Nm³; tar contents below this limit were never reached with dolomites by these authors.[13,21] Gil et al.[10] considered using a bed of dolomite downstream of the gasifier for tar reduction as the most well-known and used method. This method has higher costs than the in situ use of dolomite and gives higher tar reductions.

2.1.2. Olivine. Olivine consists mainly of silicate mineral in which magnesium and irons cations are set in the silicate tetrahedral.[22] Natural olivine is represented by the formula $(Mg,Fe)_2SiO_4$. Table 5 gives the chemical composition of a selected commercial olivine.[23]

The catalytic activity of olivine for tar elimination can be related to the magnesite (MgO) and iron oxide (Fe_2O_3) contents, where the latter is much higher in olivine than in dolomite. On this basis, the reactions involved in tar elimination with olivine should be similar to those involved in the same process with calcined rocks. This catalyst is mainly deactivated by the formation of coke, which covers the active sites and reduces the surface area of the catalyst.

The advantages of this catalyst are its low price (similarly to dolomite) and high attrition resistance compared to dolomite. Its mechanical strength is comparable to that of sand, even at high temperatures. Its performance is therefore better than that of dolomite in fluidized-bed environments.[22] Its catalytic activity for tar elimination however, is lower than dolomite.[24] Olivine is available on the market at a price about 120 Euro per metric ton.[22]

Only a small amount of research has been done on the catalytic activity of olivine for tar elimination. Rapagná et al.[22] tested olivine and dolomite in the steam gasification of biomass in a fluidized bed. They reported that the activity of olivine is comparable to that of dolomite in terms of the destruction of tars and the

Table 6. Chemical Compositions of Two Clay Materials[26]

oxide	kaolinite	montmorillonite
SiO_2	45.20	53.20
Al_2O_3	37.02	16.19
Fe_2O_3	0.27	4.13
FeO	0.06	–
MgO	0.47	4.12
CaO	0.52	2.18
K_2O	0.49	0.16
Na_2O	0.36	0.17
TiO_2	1.26	0.20
H_2O	14.82	23.15
total	100.47	100.50

resulting increase of permanent gases. Courson et al.[24] integrated a small amount of nickel into natural olivine. They found that, at 750 °C, this catalyst has a high activity in dry reforming (95% methane conversion) and steam reforming (88% methane conversion). At 770 °C, the average tar content is decreased from 43 g/Nm³ dry gas with sand to 0.6 for dolomite and 2.4 for olivine.[24] Because of olivine's mechanical strength and catalytic activity, Rósen et al.[25] used it as a bed material for the pressurized gasification of birch.

2.1.3. Clay Minerals. Most common clay minerals belong to the kaolinite, montmorillonite, and illite groups. The chemical compositions of kaolinite and montmorillonite are reported in Table 6.[26]

Wen et al.[26] related the catalytic activity for tar elimination of such materials to the (a) effective pore diameter, (b) internal surface area, and (c) number of strongly acidic sites. The catalytic activity increases with pore diameter greater than 0.7 nm, larger internal surface area, and larger number of strongly acidic sites. Simell et al.[5] reported that these materials enhance the tar cracking reaction explained by eq 3[18] and have little effect on other gas-phase reactions such as the water–gas shift reaction explained by eq 5 and the steam and dry reforming reactions explained by eqs 1 and 2. Adjaye et al.[27] reported that silica–alumina catalyst is amorphous (noncrystalline) and contains acid sites. Most of these sites are buried in inaccessible locations, thus leading to low acidity. Simell et al.[5] reported that, at temperatures above 850 °C, most aluminum silicates seem to lose their catalytic activity and act as inert materials.

The advantages of clay minerals are that they are relatively cheap and have fewer disposal problems because they can be disposed after simple treatment. The main disadvantages of these catalysts are the lower activity compared to dolomite and nickel-based catalysts and thet fact that most natural clays do not support the high temperatures (800–850 °C) needed for tar elimination (they lose their pore structure).

Simell et al.[5] tested the activity of silica–alumina (13 wt % Al_2O_3, 86.5 wt % SiO_2, 100 m²/g surface area) in a fixed bed at 900 °C and 0.3-s residence time for tar elimination of a tarry fuel gas from an updraft gasifier. They found the following order of activity: commercial nickel catalyst (Ni on Al_2O_3) > dolomite > activated alumina > silica–alumina (clay mineral) > silicon carbide (inert). Wen et al.[26] found that kaolinites and montmorillonite, which have specific surface areas of 15–20 m²/g, are catalytically less active in the catalytic pyrolysis of coal tar than very effective zeolites with pore size greater than 0.7 nm and surface areas of 600–900 m²/g. They exhibited catalytic activities similar to those of zeolites with small pore sizes.

Table 7. Main Iron Minerals[28]

mineral	CAS registry number	chemical name	chemical formula	iron (wt %)
hematite	1309-37-1	ferric oxide	Fe_2O_3	69.94
magnetite	1309-38-2	ferrous–ferric oxide	Fe_3O_4	72.36
goethite	1310-14-1	hydrous iron oxide	$HFeO_2$	62.85
siderite	14476-16-5	iron carbonate	$FeCO_3$	48.20
ilmenite	12168-52-4	iron titanium oxide	$FeTiO_3$	36.80
pyrite	1309-36-0	iron sulfide	FeS_2	46.55

2.1.4. Iron Ores. Minerals containing appreciable amounts of iron can be grouped according to their chemical compositions into oxides, carbonates, sulfides, and silicates. Table 7 lists the main iron minerals commonly used as a source of iron.[28] However, oxide minerals are the most important source of iron, and the others are of minor importance.

Metallic iron (reduced form) catalyzes tar decomposition more actively than the oxides.[29,30] Simell et al.[30] reported that iron catalyzes the reactions of the main components of fuel gas (H_2, CO, CO_2, H_2O) such as the water–gas shift reaction. Various forms of iron are reported to catalyze coal gasification reactions, pyrolysis, and tar decomposition. Iron is rapidly deactivated in the absence of hydrogen because of coke deposition.[29] Simell et al.[17] tested the activities of two ferrous materials in catalyzing the decomposition of tarry constituents in fuel gas in a tube reactor in the temperature range of 700–900 °C. The ferrous materials tested were iron sinter and pellet in which iron exists as magnetite (Fe_3O_4) and, in smaller amounts, as hematite (Fe_2O_3).The activities of these materials were found to be lower than that of dolomite. Tamhankar et al.[29] studied the catalytic cracking activity and reaction mechanism of benzene on iron oxide–silica. They found that the catalyst in its reduced form has a high activity toward benzene cracking and a high selectivity toward methane formation. They found also that hydrogen plays a critical role in the overall reaction and in suppressing catalyst deactivation. Cypers et al.[31] studied the influence of iron oxides on coal pyrolysis. They found that the presence of iron oxides reduces the tar yield in the coal primary devolatilization zone between 300 and 600 °C. The production of methane increases toward the end of the devolatilization zone of coal in the presence of iron oxide. They found that hematite has a greater effect than magnetite.

2.2. Synthetic Catalysts. Synthetic catalysts are chemically produced and relatively more expensive than the mineral catalysts.

2.2.1. Char. Char is a nonmetallic material. It can be produced by the pyrolysis of coal or biomass. In the usual carbonization procedure, heat at 400–500 °C is applied for a prolonged period of time in the absence of air. The proximate and ultimate analysis of two types of chars is reported in Table 8.

The catalytic activity of char for tar elimination can be related to the pore size, the surface area, and the ash or mineral content of the char. The first two factors are dependent on the char production method, such as the heating rate and the pyrolysis temperature. The last factor depends mainly on the char precursor type. The char is deactivated by (a) coke formation, which blocks the pores of the char and reduces the surface area of the catalyst, and (b) catalyst loss, as char can be gasified by the steam and dry reforming reactions explained by eqs 1 and 2.

Table 8. Proximate and Ultimate Analyses of Chars Produced from Charcoal and Poplar Wood[32,33]

	char from poplar wood[32]	char from charcoal[33]
proximate dry analysis (wt %)		
ash	4.6	1
volatiles	7.4	9.4
ultimate analysis (wt %)		
C	85.5	92
H	0.76	2.45
O	8.9	3
N	0.29	0.53
S	−	1
total	100	100

Table 9. Wood Ash Analysis after Gasification[12]

component	wt %
CaO	44.3
MgO	15
K_2O	14.5

The attractiveness of char as a catalyst originates from its low price and its natural production inside the gasifier. However, it can be consumed by gasification reactions with steam or CO_2 in the producer gas, and therefore, a continuous external supply is needed.

Zanzi et al.[34] studied the effect of the rapid pyrolysis conditions on the reactivity of char in gasification. They found that the reactivity of char produced in the pyrolysis stage is highly affected by the treatment conditions, and they thought it might significantly increase if high heating rates, small fuel particle sizes, and short residence times at high temperatures were used. Chembukulam et al.[35] found that the conversion of tar and pyroligneous liquor over semicoke/charcoal at 950 °C resulted in almost complete decomposition into gas of low calorific value. Seshardi et al.[36] studied the conversion of a coal liquid (tar) over a char−dolomite mixture under different temperatures, pressures, and carrier gases. Chembukulam et al.[35] found that the conversion of tar and pyroligneous liquor over semicoke/charcoal at 950 °C resulted in almost complete decomposition into gas of low calorific value.

2.2.2. Fluid Catalytic Cracking (FCC) Catalysts. Zeolites represent a well-defined class of crystalline aluminosilicate minerals whose three-dimensional structures are derived from frameworks of $[SiO4]^{4-}$ and $[AlO4]^{5-}$ coordination polyhedra.[37] Catalytic cracking is a process that breaks down the larger, heavier, and more complex hydrocarbon molecules into simpler and lighter molecules by the action of heat and aided by the presence of a catalyst but without the addition of hydrogen. In this way, heavy oils (fuel oil components) can be converted into lighter and more valuable products (notably LPG, gasoline, and middle distillate components). The catalytic cracking of hydrocarbons is believed to be a chain reaction that follows the carbenium ion theory developed by Whitmore.[38] His mechanism involves three steps:[39,40] initiation, propagation, and cracking.

The acidic properties (Brønsted sites) of zeolites are dependent on the method of preparation, the form, the temperature of dehydration, and the Si/Al ratio. The key properties of zeolites are structure, Si/Al ratio, particle size, and nature of the (exchanged) cation. These primary structure/composition factors influence acidity, thermal stability, and overall catalytic activity.

The catalytic behavior of FCC catalysts differs from that of the previously described catalysts that have low surface acidity or are considered basic, such as calcined rocks. FCC catalysts are used mainly to perform tar cracking reactions, which can be summarized by the general reaction given in eq 7. However, de Tânia et al.[41] found that zeolites might be appropriate catalysts for the water−gas shift reaction given by eq 5. Seshardi

et al.[36] related the activity of zeolites in cracking coal liquid to their large surface areas, large pore diameters, and high densities of acid sites. The loss of catalytic activity is mainly related to coke formation and substances whose molecules react with the catalyst acidic sites. Coke decreases the surface area and the zeolite micropore volume by blocking its channels. Steam, basic nitrogen compounds, and alkaline metals react with the catalyst acidic sites and poison the catalyst.

The advantages of these catalysts are related to their relatively low price and the knowledge gained about them from long experience with their use in FCC units. The major disadvantage of these catalysts is their rapid deactivation because of coke formation.

Radwan et al.[42] characterized the coke deposited from benzene cracking over USY zeolites in the temperature range of 500−800 °C under He or H_2 gas flow at 1.0 and 5.0 MPa. They found that the composition of coke strongly depends on the cracking temperature and that the H/C ratio decreases with increasing temperature. Adjaye et al.[27] examined the relative performance of HZSM-5, H-mordenite, H−Y, silicalite, and silica−alumina in the production of the organic distillate fraction (ODF); the formation of hydrocarbons; and the minimization of char, coke, and tar formation. They found that HZSM-5 was the most effective catalyst for the production of ODF, overall hydrocarbons, and aromatic hydrocarbons. In addition, it provided the least coke formation. Silica−alumina catalyst was most effective in minimizing char formation. H−Y catalyst was superior in minimizing tar formation as well as maximizing aliphatic hydrocarbon production. Gil et al.[10] tested a spent catalyst "in equilibrium" in a fluidized bed and found that the FCC catalyst was quickly elutriated from the bed. Herguido et al.[43] tested a spent FCC catalyst in equilibrium in a 15-cm-i.d. riser−gasifier with a stable fluidized bed of sand at its bottom. Tar was reduced from 78 to 9 g/Nm^3 with recirculation and continuous regeneration of the catalyst.

2.2.3. Alkali Metal-Based Catalysts. Alkali metals are any of the monovalent metals lithium (Li), sodium (Na), potassium (K), rubidium (Rb), cesium (Cs), and francium (Fr), belonging to group 1A of the periodic table. They are all highly reactive and electropositive. Alkali metals, principally K and to a lesser extent Na, exist naturally in biomass.[44] Their salts are soluble and gained from ashes of plants.[11] Table 9 shows the analysis of wood ash after gasification as reported by Sutton et al.[12] To reduce the tar content, these ashes can be used as primary (in situ) or secondary (outside the gasifier) catalysts. On the other hand, they can be used directly as catalysts in the form of alkali metal carbonates or supported on other materials such as alumina. Direct addition of alkali materials to biomass is done by dry mixing or wet impregnation.

Alkali metals catalyze gasification reactions. They are considered as effective catalysts for H_2O and CO_2 gasification of carbon.[45] Padban[46] reported that alkali metals, especially K, act as promoters in unzipping the cellulose chains during the thermal decomposition of woody biomass. Lizzio et al.[47] reported that K is a good

Table 10. Main Minerals Containing Aluminum Oxide[51]

mineral	CAS registry number	formula
aluminum hydroxide	21645-51-2	$Al(OH)_3$
bauxite	1318-16-7	
boehmite	1318-23-6	$AlO(OH)$
corundum	1302-74-5	α-$Al2O_3$
diaspore	14457-84-2	α-$AlO(OH)$
gibbsite	14762-49-3	α-$Al(OH)_3$
sapphire	1317-82-4	Al_2O_3

catalyst for the steam gasification of coal because of the formation of a liquid–solid interface between K and carbon. The same authors explained that, when K_2CO_3 is used as the K precursor, it wets and is dispersed well on the coal surface. These catalysts lose their activity because of particle agglomeration when added to biomass in fluidized-bed gasifiers.[12] They also lose their activity at high temperatures (900 °C) when used in secondary fixed beds because of melting and agglomeration.[48] Lizzio et al.[47] related the deactivation of K during gasification to several factors including the loss of contact between the catalyst and char, particle sintering, unfavorable reaction with the mineral matter of char, and loss of potassium by vaporization.

The advantage of alkali metals as catalysts comes from their natural production in the gasifier where ashes are produced. The use of ashes as catalysts solves the problem of the handling of ash wastes and gives an added value to the gasification process by increasing the gasification rate and reducing the tar content in the produced gas. However, the major disadvantage of these catalysts is their loss of activity due to particle agglomeration.

Sutton et al.[12] reported several disadvantages for the direct addition of alkali metal catalysts, such as difficult and expensive recovery of the catalyst, increased char content after gasification, and ash disposal problems. Lee et al.[49] found that the addition of Na_2CO_3 enhances the catalytic gasification of rice straw over nickel catalyst and significantly increases the formation of gas. The same authors found that the formation of gas depends on the nature of the alkali metal carbonate used and has the order Na ≥ K > Cs > Li. Sutton et al.[12] reported that K_2CO_3 is not suitable as a secondary catalyst because the hydrocarbon conversion rarely exceeds 80% when it is used. Lee et al.[50] found that the catalytic activity of single salts in steam gasification depends on the gasification temperature, with the following order of activity: K_2CO_3 > $Ni(NO_3)_2$ > K_2SO_4 > $Ba(NO_3)_2$ > $FeSO_4$.

2.2.4 Activated Alumina. Activated alumina consists of a series of nonequilibrium forms of partially hydroxylated aluminum oxide, Al_2O_3. Its chemical composition can be represented by $Al_2O_{(3-x)}(OH)_{2x}$, where x

ranges from about 0 to 0.8. The porous solid structure of activated alumina is produced by heating (calcining) the hydrous alumina precursor to drive off the hydroxyl groups.[51] Aluminum oxide can be found in several minerals as indicated in Table 10.

The catalytic activity of alumina is related to the complex mixture of aluminum, oxygen, and hydroxyl ions that combine in specific ways to produce both acid and base sites.[51] Activated alumina is deactivated by coke formation.

The advantage of activated alumina is its relatively high activity, which is comparable to that of dolomite.[17] The main disadvantage is rapid deactivation by coke compared to dolomite (personal communication with Corella and Simell, 2003).

Simell et al.[17] tested the activity of activated alumina (99 wt % Al_2O_3) in catalyzing the decomposition of tarry constituents in fuel gas in a tube reactor in the temperature range of 700–900 °C. They found that activated alumina was nearly as effective as dolomite.

2.2.5. Transition Metal-Based Catalysts. Transition metals are considered as good catalysts for the steam and dry reforming of methane and hydrocarbons. Nickel catalyst supported on alumina is cheaper and sufficiently active than other metals such as Pt, Ru, and Rh.[52] Nickel metal is one of the group VIII metals. The general composition of the Ni-based catalysts can be divided into three main components: (a) Ni element, (b) support, and (c) promoters. The Ni represents the active site of the catalyst. The support material gives the catalyst mechanical strength and protection against severe conditions such as attrition and heat. Alumina-based materials are considered the primary support material for most reforming catalysts. Promoters such as alkaline earth metals, e.g., magnesium (Mg), and alkali metals, e.g., potassium (K), are added to ensure economical operations under severe conditions. Mg is used to stabilize the Ni crystallite size and K to neutralize the support surface acidity and thereby reduce coke deposition on the catalyst surface and enhance catalyst activity.[53] In general, the steam-reforming catalysts can be classified into two types according to the feed: (a) light hydrocarbons (particularly methane) and (b) heavy hydrocarbons (particularly naphtha). Table 11 provides examples of the composition of eight commercial Ni-based steam-reforming catalysts used by Caballero et al.[54] The first four are for light hydrocarbons, and the last four (unidentified) are for the heavy hydrocarbons.

Steam-reforming catalysts exhibit high activities for tar elimination and gas upgrading in biomass gasification. These catalysts accelerate steam and dry reforming reactions (eqs 1 and 2), and water–gas shift reaction (eq 5). Aznar et al.[55] found that heavy-hydrocarbon

Table 11. Compositions of Some Commercial Ni-Based Steam-Reforming Catalysts[54]

company	catalyst	composition (wt %)									
		NiO	Al_2O_3	CaO	SiO_2	K_2O	$MgAl_2O_4$	MgO	Fe_2O_3	MnO	BaO
United Catalysts	C11-9-061	10−15	80−90	<0.1	<0.05				1−5	1−5	1−5
Haldor Topsoe	RKS-1	15			0.1	a	85				
ICI	57-3	12	78	10	0.1						
BASF	G1-25S	12−15	>70		<0.2						
	nickel A	22	26	13	16	7		11			
	nickel B	15			0.1	a	85				
	nickel D	20			<0.2						
	nickel E	25	>70		<0.2	1					

[a] <500 ppm.

Table 12. Summary of Catalysts Advantages and Disadvantages

catalyst	advantages	disadvantages
calcined rocks	inexpensive and abundant attain high tar conversion ~95% conversion with dolomite often used as guard beds for expensive catalysts most popular for tar elimination	fragile materials and quickly eroded from fluidized beds
olivine	inexpensive high attrition resistance	lower catalytic activity than dolomite
clay minerals	inexpensive and abundant fewer disposal problems	lower catalytic activity than dolomite most natural clays do not support the high temperatures (800–850 °C) needed for tar elimination (lose pore structure)
iron ores	inexpensive abundant	rapidly deactivated in the absence of hydrogen lower catalytic activity than dolomite
char	inexpensive natural production inside the gasifier high tar conversion comparable to dolomite	consumption because of gasification reactions
FCC	relatively inexpensive but not cheaper than the above more known about it from experience with FCC units	rapid deactivation by coke lower catalytic activity than dolomite
alkali-metal-based	natural production in the gasifier reduce ash-handling problems	particle agglomeration at high temperatures lower catalytic activity than dolomite
activated alumina	high tar conversion comparable to that of dolomite	rapid deactivation by coke
transition-metal-based	able to attain complete tar elimination at ~900 °C increase the yield of CO_2 and H_2 Ni-based catalysts are 8–10 times more active than dolomite	rapid deactivation because of sulfur and high tar content in the feed relatively expensive

steam-reforming catalysts are more active than light-hydrocarbon steam-reforming catalysts. The activity of these catalysts depends on the nickel content, support type, and the promoter(s) type and content.

Ni-based catalysts can be deactivated in several ways, which can be summarized as follows: (a) Mechanical deactivation normally occurs because of loss of catalytic material through attrition and loss of surface area through crushing. This deactivation is irreversible and can be prevented by selecting less severe process conditions. Fluidized-bed conditions increase catalyst attrition and mechanical deactivation, so these catalysts are normally used in fixed beds.[56] (b) Sintering causes loss of surface area and occurs as a result of severe conditions such as high temperatures. (c) Fouling occurs as a result of physical blockage of the catalyst surface area by coke. Such deactivation is usually reversible and can be reduced or prevented by conditioning the feed gas. Baker et al.[15] reported that the catalyst support acidity affects coke accumulation and catalyst deactivation, with higher support acidity increasing the cracking reaction described by eq 3. Catalytic deactivation due to fouling is also a function of catalyst placement and the mode of contact (fixed or fluidized bed). [15] Aznar et al.[55] proposed that the tar content in the fuel gas entering a bed of Ni-based catalyst has to be below 2 g/Nm[3] to avoid catalyst deactivation by coke. (d) Poisoning is caused by the strong chemisorption onto the catalyst active sites of impurities (mainly H_2S) in the feed. Engelen et al.[57] reported that typical biomass gasification gas contains 20–200 ppm H_2S, depending on the solid fuel used. Poisoning can be prevented by conditioning the feed gas to the catalyst. Sulfur poisoning is reversible and has a temporary effect on the catalyst.[58] Hepola et al.[58] reported that, at 900 °C, the activity of the Ni catalyst recovered rapidly when H_2S was removed from the gas. Forzatti et al.[59] reported that

S adsorption decreases with increasing temperature. They reported that 5 ppm sulfur in the feed poisoned a Ni/Al_2O_3 steam-reforming catalyst working at 800 °C, whereas less than 0.01 ppm poisoned the same catalyst working at 500 °C.

The main advantages of Ni-based catalysts are their ability to attain complete tar elimination at temperatures of around 900 °C[60] and to increase the yields of CO and H_2.[54] Olivares et al.[61] reported that commercial nickel-based catalysts are 8–10 times more active than calcined dolomites under the same operating conditions. The disadvantages of these catalysts are their rapid deactivation from sulfur and high tar contents in the feed and the need for preconditioning of the feed before it enters the catalyst bed. In addition, such catalysts are relatively expensive.

Ni-based catalysts have proven to be useful in biomass gasification for gas cleaning and upgrading.[52] Sutton et al.[12] reported that the use of Ni-based catalysts at temperatures higher than 740 °C generally results in an increase in the H_2 and CO contents, with a decrease in the hydrocarbon (tar) and methane contents. Aznar et al.[55] found that steam-reforming catalysts for heavy hydrocarbons (naphtha) are more active for tar elimination than commercial steam-reforming catalysts for light hydrocarbons (methane). Arauzo et al.[62] studied the catalytic pyrogasification of biomass in a fluidized-bed reactor. They found that the addition of Mg in the catalyst crystal lattice improved the resistance to attrition and loss in gasification activity due to increased coke production. However, the same authors found that the addition of potassium had little effect. Lee et al.[49] found that the addition of Na_2CO_3 to a nickel catalyst significantly enhances its activity for the catalytic gasification of rice straw and also significantly increased gas formation. Baker et al.[18] explored the effect of the gas–solid contact mode and

placement of the catalyst on the performance of a Ni-based catalyst. They found poor catalyst performance due to coke deactivation if the catalyst is placed in the gasifier or in a secondary fixed bed, compared to catalyst placement in a secondary fluidized bed. Yamaguchi et al.[63] tested the performance of alumina-supported nickel catalysts for the steam gasification of wood. They found that the activity of the catalyst decreased over time due to coke fouling and sintering of the nickel metal in the catalyst. Hepola et al.[58] reported that the performance of a nickel-based catalyst for tar elimination decreased as a result of H_2S adsorption whereas the ammonia conversion seemed to be enhanced by H_2S concentrations in the gas. The authors found that high operating temperatures reduced the catalyst deactivation caused by H_2S.

3. Summary of Catalyst Review

This survey presents a review of the various types of catalysts that have been used in several research directed toward reducing the tars in the producer gas from the gasification process. It also suggests a classification for catalysts into minerals and synthetic catalysts. This classification is based on the catalyst production method. The advantages and disadvantages of the different catalysts are summarized in Table 12.

Further research needs to be done in the following areas: (a) The catalytic activity of olivine should be investigated. No significant research has been done on it, even though it seems promising. (b) The possibility of reducing coke formation on silica−alumina should also be studied. The catalytic activity of silica−alumina is comparable to that of dolomite, but faster coking reduces its potential. (c) The catalytic activity of char for tar elimination should be characterized. Char shows good catalytic activity for tar elimination, which is noticed in downdraft gasifiers. (d) Also in need of study are the stability of FCC catalysts at high temperatures and the effect of steam and other components in the producer gas on the performance of FCC catalysts. (e) In the next stage of our project, screening of catalysts will be carried out in a fixed-bed tubular reactor. The catalytic activities of olivine, char, and FCC catalysts will be tested taking in consideration the above-mentioned points.

Acknowledgment

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