I&EC research
Industrial & Engineering Chemistry Research

Review

Cite This: Ind. Eng. Chem. Res. 2019, 58, 7690−7705

pubs.acs.org/IECR

Catalytic Cracking of Biomass-Derived Hydrocarbon Tars or Model Compounds To Form Biobased Benzene, Toluene, and Xylene Isomer Mixtures

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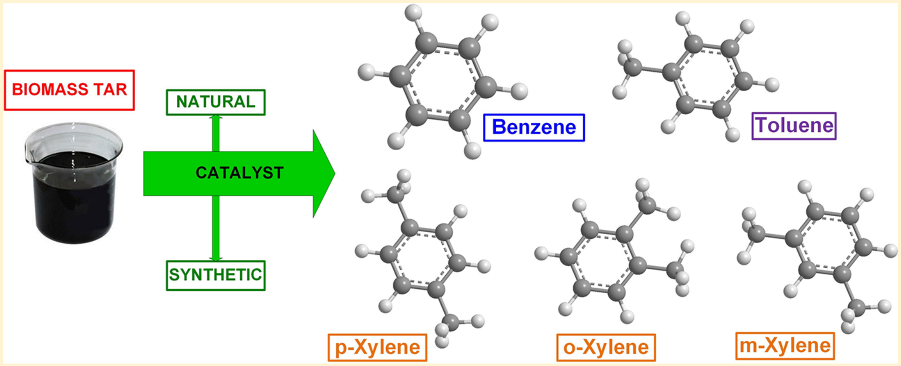
Supporting Information



ABSTRACT: The gasification of biomass is one of the most prominent technologies for the conversion of the raw material feedstock to polymers, useful chemical substances, and energy. The main engineering challenge during the processing of wastes is the presence of tars in gaseous reaction products, which could make this operation methodology unsuccessfully due to the blockage of separating particle filters, fuel line flow, and substantial transfer losses. Catalytic hydrocarbon cracking appears to be a promising developing approach for their optimal removal. However, it is still highly desirable to enhance the catalysts' activity kinetics, selectivity, stability, resistance to (ir)reversible coke deposition, and regeneration solutions. The purpose of this Review is to provide a comparative systematic evaluation of the various natural, synthetic, and hybrid ways to convert the model molecular compounds into benzene, toluene, xylene, (poly)aromatics, syngas, and others. The recent scientific progress, including calcite, dolomite, lime, magnesite, olivine, char, nonmetallic activated carbons, supported alkali, noble, and transition metals, and (metal-promoted) zeolites, is presented. A special concentrated attention is paid to effectiveness, related to hydrogenation, peculiar pore structure, and formulations' suitable acidity. The role of catalysis is described, recommendations for prospective catalyzed mechanisms are provided, and future technical feasibility is discussed as well.

1. INTRODUCTION

Today, alternative renewable energy has a promising potential and was extensively studied in recent years due to fossil fuel depletion, global warming, and serious problems related to environmental pollution.[1,2] Biomass is one of the main alternative renewable energy sources together with solar and wind energy, where the latter two are less reliable due to the fluctuation of wind and sunlight availability.[3,4]

Biomass is a biological material which stores energy through photosynthesis process in the presence of sunlight and basically derived from living organism like plants, crop residues, animals, etc.[5] Biomass consists of a wide range of organic materials, which are generally composed of cellulose, hemicellulose, lignin, lipids, proteins, simple sugars, starches, inorganic constituents, and a fraction of water. Biomass that mainly consists of cellulose, hemicellulose, and lignin is often referred to as lignocellulosic (LC) biomass.[6] The dry weight of typical biomass includes 51 wt% of carbon, 42 wt% of oxygen, 5 wt% of hydrogen, 0.9 wt% of nitrogen, and 0.01−2 wt% of chlorine.[6,7]

The technologies for biomass conversion into chemical intermediates (sugars, organic acids), commodity chemicals (solvents, lubricants, surfactants, adhesives, inks), fine chemicals (pharmaceuticals, nutraceuticals), and materials (renewable plastics, natural fibers) are based on four main routes: direct combustion, physical conversion, biochemical conversion, and thermochemical conversion (Figure 1).[8,9] In the biochemical conversion route, the biomass is converted into ethanol, acetone, butanol, hydrogen, or methane by aerobic fermentation or anaerobic digestion.[9] The thermochemical conversion route has some advantages over the

Received: March 4, 2019
Revised: April 18, 2019
Accepted: April 23, 2019
Published: April 23, 2019

DOI: 10.1021/acs.iecr.9b01219

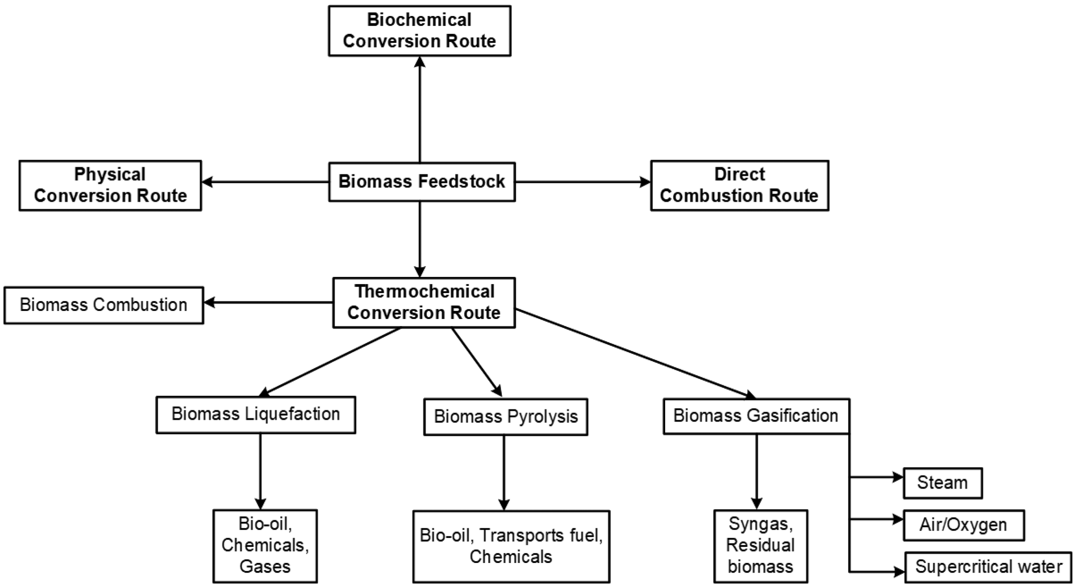


Figure 1. Biomass conversion routes. Adapted from refs 5 and 9.

biochemical conversion route, such as the unrestricted type of feedstock that can be used and fast process rate. Furthermore, the thermochemical conversion route includes combustion, liquefaction, pyrolysis, and gasification technologies. Among them, biomass gasification is advantageous due to higher energy recovery and heat capacity.[5]

2. BIOMASS GASIFICATION

Biomass can be converted to syngas, liquid biofuels, and biochar by thermochemical processes such as combustion, pyrolysis, and gasification.[10] Among these three thermochemical conversion routes (Figure 1), gasification is a self-sufficient autothermic process in terms of an energy balance.[5] In addition, biomass gasification is a promising technology due to the production of syngas mixtures composed of H_2, CO, CO_2, H_2O, and various light hydrocarbons (C_xH_y).[10−12] Figure 2 shows that biomass gasification involves a great number of complex and closely interconnected thermochemical processes, which includes upstream processing, gasification, and downstream processing.[13]

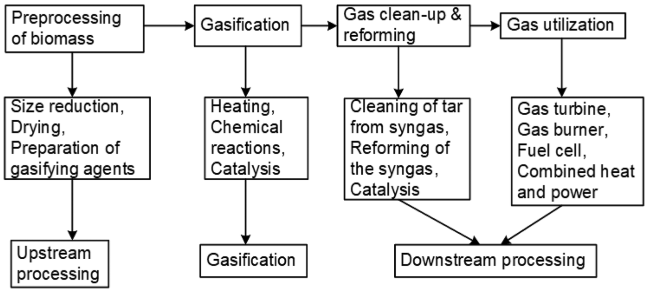


Figure 2. Processes involved in biomass gasification. Adapted from refs 13 and 14.

The main reactions (eqs 1−13) that occur during biomass gasification can be summarized as follows:[2,6,9,15−17]

Boudouard reaction:

$$C + CO_2 \leftrightarrow 2CO + 172\ \text{kJ/mol} \tag{1}$$

Steam gasification:

$$C + H_2O \leftrightarrow CO + H_2 + 131\ \text{kJ/mol} \tag{2}$$

Hydrogasification:

$$C + 2H_2 \leftrightarrow CH_4 - 74.8\ \text{kJ/mol} \tag{3}$$

Oxidation reactions:

$$C + O_2 \rightarrow CO_2 - 394\ \text{kJ/mol} \tag{4}$$

$$CO + 0.5O_2 \rightarrow CO_2 - 284\ \text{kJ/mol} \tag{5}$$

$$CH_4 + 2O_2 \leftrightarrow CO_2 + 2H_2O - 803\ \text{kJ/mol} \tag{6}$$

$$H_2 + 0.5O_2 \rightarrow H_2O - 242\ \text{kJ/mol} \tag{7}$$

Water−gas shift reaction (WGS):

$$CO + H_2O \leftrightarrow CO_2 + H_2 - 41.2\ \text{kJ/mol} \tag{8}$$

Methanation reactions:

$$2CO + 2H_2 \rightarrow CH_4 + CO_2 - 247\ \text{kJ/mol} \tag{9}$$

$$CO + 3H_2 \leftrightarrow CH_4 + H_2O - 206\ \text{kJ/mol} \tag{10}$$

$$CO_2 + 4H_2 \rightarrow CH_4 + H_2O - 165\ \text{kJ/mol} \tag{11}$$

Steam reforming reactions:

$$CH_4 + H_2O \leftrightarrow CO + 3H_2 + 206\ \text{kJ/mol} \tag{12}$$

$$CO_2 + 0.5O_2 \rightarrow CO + 2H_2 - 36\ \text{kJ/mol} \tag{13}$$

For these gasification reactions, gasifying agents such as air, oxygen, steam, carbon dioxide, or their mixtures have a significant influence on the quantity and quality of the products.[9] The most utilized gasifying agent is air because it is inexpensive, but the quality of the syngas is low due to the large amount of N_2 in the air. In the case of oxygen, the cost is higher due to the energy requirements for its production, but the quality of the formed syngas is higher as well, due to the absence of N_2. The steam gasification of biomass is becoming more and more attractive recently due to the increase in the heating value of syngas.

However, during the biomass gasification process, many byproducts are generated, such as NO_x, SO_x, NH_3, alkali

DOI: 10.1021/acs.iecr.9b01219
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(mostly potassium) salts, ash, char, and tar, and those can have a negative environmental impact.[11,12,18,19] One of the main technical problems is the presence of tar, which could make this technology economically feasible from a commercial point of view.[2,20]

3. BIOMASS TAR

Several definitions of the term "tar" can be found in the literature. By summarizing all the descriptions, we can conclude that "tar" is a mixture of oxygenated organic constituents that are generated by the partial reaction of the biomass feedstock, condenses on metal surfaces at room temperature, and has a molecular weight larger than that of benzene and a boiling point higher than 150 °C.[14] Besides the main elements such as C and H, other elements like O, N, and S are found in tar.[21] The diagram in Figure 3 shows that the biomass tar is diverse and complicated, containing more than 10 000 various organic compounds, such as oxygen-containing hydrocarbons, aromatic compounds, sulfur-containing hydrocarbons, and polynuclear aromatic hydrocarbons (PAHs), where is the latter are environmental hazards with carcinogenic character.[10,20,22,23] The formation of tar during gasification processes can cause serious issues for the gasifier and the operation of downstream processes facilities, such as blocking of pipes, cracking of pipes in the filter pores, forming coke and plugging the pipes, condensing on the surface of filters, pumps, and heat exchangers, corroding the surface of the pipes, and consequently reducing the gasification efficiency.[10,20,22,24]

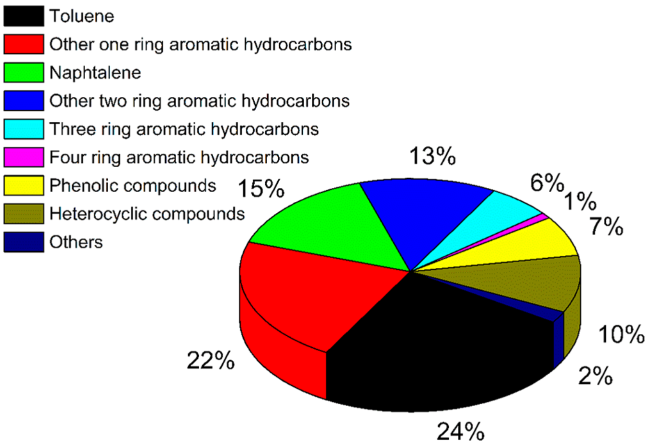


Figure 3. Typical composition of biomass tars. Adapted from refs 2, 20, 25, and 26.

There are several methods to remove tar from the syngas such as physical treatment, thermal cracking, plasma-assisted cracking, and catalytic cracking.[10,22,24] Catalytic tar cracking is considered as a highly efficient, economical, and technically viable technique for conversion of tar into combustible gas and useful chemicals.[10,24]

The decomposition of tar is carried out via the following reactions (eqs 14−20):[2,9,14,26,27]

Dry reforming:

$$C_xH_y + xCO_2 \rightarrow (y/2)H_2 + 2xCO \qquad (14)$$

Steam reforming:

$$C_xH_y + xH_2O \rightarrow (x + y/2)H_2 + xCO \qquad (15)$$

Carbon formation:

$$C_xH_y \rightarrow xC + (y/2)H_2 \qquad (16)$$

Hydrogenation:

$$C_xH_y + (2x - y/2)H_2 \rightarrow xCH_4 \qquad (17)$$

Thermal cracking and carbon formation:

$$C_xH_y \rightarrow xC + (y/2)H_2 \qquad (18)$$

$$C_xH_y \rightarrow (y/4)CH_4 + (x - y/4)C \qquad (19)$$

Partial oxidation:

$$C_xH_y + (x/2)O_2 \rightarrow xCO + (y/2)H_2 \qquad (20)$$

The model compounds as representatives of different tar classes have been frequently used for investigation and prediction of the behavior of tars.[1] The most widely investigated tar model compounds, including toluene, phenol, naphthalene, 1-methylnaphthalene, and anthracene, are presented in Table 1.[28] Toluene, naphthalene, and phenol are the most commonly used model compounds, as they are the main tar constituents. At the same time, PAHs are also often used as model compounds of tars because they are problematic pollutants in the producer gas in the gasifier and they are highly refractory.[1,29−31]

Evans and Milne[33] classified the composition of tar from biomass pyrolysis and gasifier units into four major types as a result of gas-phase thermal cracking reactions:

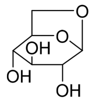
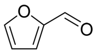
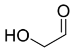
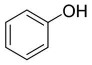
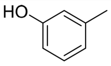
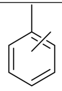
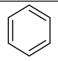
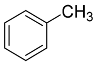
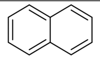
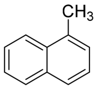
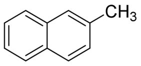
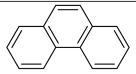
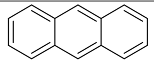
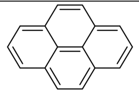
- Primary tars: characterized by cellulose-derived products such as levoglucosan, hydroxyacetaldehyde, and furfurals;
- Secondary tars: characterized by phenolics and olefins;
- Tertiary tars: include methyl derivatives of aromatics, such as methyl acenaphthylene, methylnaphthalene, toluene, and indene;
- Condensed tertiary products: show the PAHs series without substituents (benzene, naphthalene, acenaphthylene, anthracene/phenanthrene, pyrene).

Figure 4 shows the transition of tars as a function of process temperature.[21] The composition of tar is changed based on the feedstock, the type of gasifier, and the gasification temperature. The main compounds of tar are changed from oxygenates with low molecular weight to light and heavy hydrocarbons with the increase of gasification temperature from 400 to 1000 °C.[15]

4. CATALYSTS FOR BIOMASS TAR CRACKING

The cracking of biomass tar over heterogeneous catalysts can produce basic feedstocks for the petrochemical industry.[34] Now, benzene, toluene, and xylene (BTX) aromatics have an increasing number of industrial applications where benzene is primarily used for production of ethylbenzene, cumene, cyclohexane, nitrobenzene, alkylbenzene, chlorobenzenes, styrene, phenol, nylon, etc.[35] Toluene is used for gasoline blending for its octane number boosting and for production of nitrotoluenes, solvents, toluene diisocyanate, explosives, dyes, etc.[36] Xylenes can either be applied in refinery streams for gasoline blending or can be separated into *o*-xylene, *p*-xylene, and *m*-xylene isomers or converted to other chemicals such as phthalic anhydride, isophthalic acid, terephthalic acid, polyesters, alkyd resins, etc. According to Omran et al.,[37] in 2017 the global prices were as follow: benzene, \$1.30/kg; toluene, \$1.27/kg; *p*-xylene, \$1.53/kg, and mixed xylenes, \$1.30/kg. At the same time, the market price of syngas (e.g.,

Table 1. Common Tar Model Compounds[a]

Model tar	Tar class	Formula	Structure
Levoglucosan	Primary	$C_6H_{10}O_5$	
Furfural	Primary	$C_5H_4O_2$	
Hydroxyacetaldehyde	Primary	$C_2H_4O_2$	
Phenol	Secondary	C_6H_6O	
Cresol	Secondary	C_7H_8O	
Xylene	Secondary	C_8H_{10}	
Benzene	Tertiary	C_6H_6	
Toluene	Tertiary	C_7H_8	
Naphthalene	Tertiary	$C_{10}H_8$	
1-Methylnaphthalene	Tertiary	$C_{11}H_{10}$	
2-Methylnaphthalene	Tertiary	$C_{11}H_{10}$	
Phenanthrene	Tertiary	$C_{14}H_{10}$	
Anthracene	Tertiary	$C_{14}H_{10}$	
Pyrene	Tertiary	$C_{16}H_{10}$	

[a]Adapted from refs 1 and 32.

obtained from glycerol) is less than \$0.1/kg,[38] which points to the prospects for BTX production from biomass tar.

Figure 5 shows that many different natural and synthetic heterogeneous catalysts such as olivine, dolomite, char, activated carbons, zeolites, metal-promoted zeolites, noble, alkali, and transition metal catalysts have been investigated for catalytic cracking of biomass tar into syngas or BTX product mixture.[10] According to Claude et al.,[25] the catalyst deactivation from coke formation during the biomass tar removal is the most significant issue that catalytic materials have to confront, since carbon deposits decrease the activity of the metallic active sites and can block the support pores that are responsible for the high active surface area.

The main characteristics of a suitable catalyst for biomass-derived tar catalytic cracking are as follows:[2,25,39]

1. High activity and efficiency on tar removal in environments that contain high concentrations of H_2, CO, CO_2, H_2O in the temperature range of 500−900 °C;
2. High CH_4 reforming activity when the focus is the H_2 production;
3. High resistance to coking, poisoning, and sintering;
4. Easy regeneration;
5. Strong resistance to attrition;

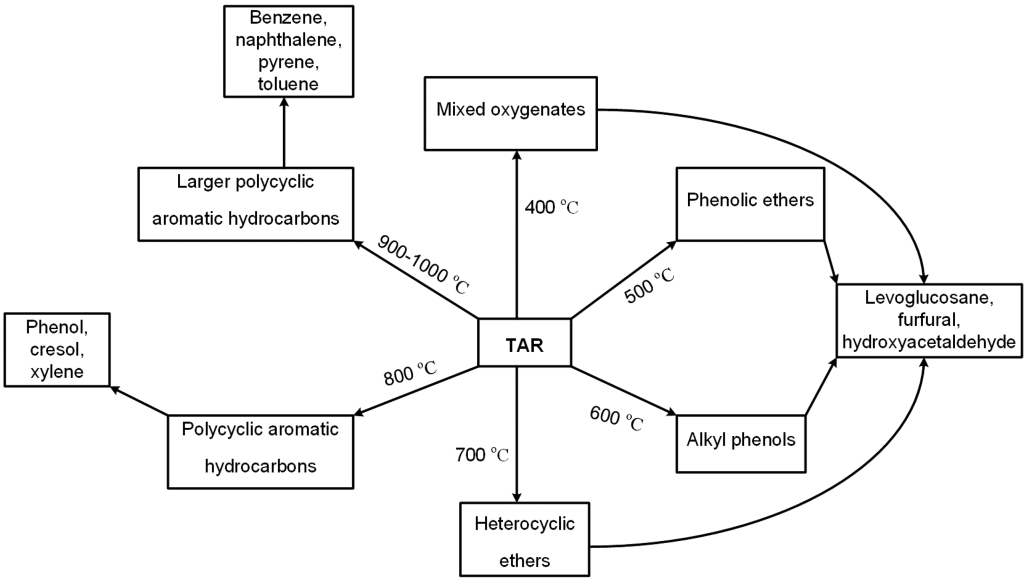


Figure 4. Transition of tars dependent on the temperature. Adapted from refs 14, 15, 21, 25, and 33.

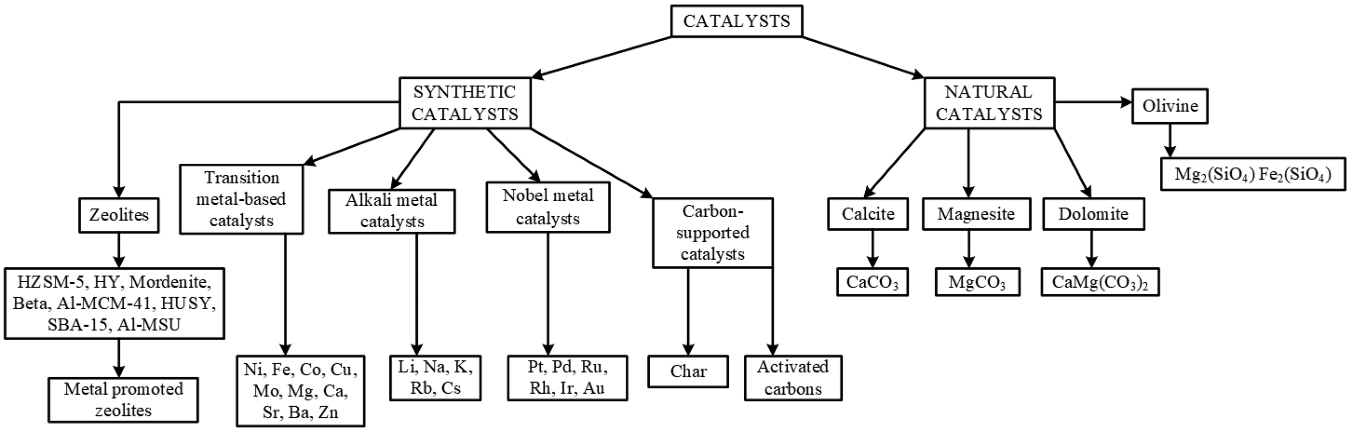


Figure 5. Types of catalysts used for tar conversion. Adapted from refs 20 and 25.

6. Commercial availability and price;
7. Environmental suitability.

Thus, we can conclude that a suitable catalyst with all these parameters can successfully convert tars and increase the economic feasibility of the biomass gasification process.

4.1. Natural Catalysts. Natural mineral catalysts such as dolomite, calcite, magnesite, olivine, clay minerals, and sea shells can be used as catalysts directly or with some physical treatment (such as heating) but without chemical treatment.[9] The catalysts fitting into this class are naturally available. In general, it can be noted that natural catalysts are relatively cheap compared to synthetic catalysts.[20] The most widely used and studied natural catalysts are dolomite and olivine.

4.1.1. Dolomite. The main advantages of calcined rock materials are the low cost and abundance.[20] Dolomite is a calcium–magnesium ore with some minor impurities and the general chemical formula $CaMg(CO_3)_2$, composed of a mixture of calcium carbonate and magnesium carbonate at a concentration ratio of nearly 1:1.[2,40,41] In order for dolomite to become active for tar conversion, a calcination step that eliminates CO_2 and transforms $CaMg(CO_3)_2$ into active CaO and MgO is required. CaO exhibits higher activity than MgO, but their interaction with each other has a synergistic effect resulting in higher activity of dolomite in a tar cracking reaction compared to individual constituents.

Many research groups have extensively studied dolomites because of its highly effective tar conversion.[23,42−46] Corella et al.[44] showed that tar content at the gasifier outlet was approximately 40% lower using dolomite compared to natural olivine. Moreover, dolomite was 1.4 times more active than olivine in biomass gasification with air but at the same time dolomite generates 4–6 times more particulates as well as more NH_3 in the product compared to olivine. Andrés and co-workers[45] reported that dolomite has the highest activity in tar elimination, followed by alumina and olivine. Boot-Handford and co-authors[46] observed that calcined dolomite was slightly more effective in biomass-derived tar cracking than calcined limestone, converting 98 wt% of the tar at 900 °C. Recently, Yu and co-workers[23] compared 0.5% Ni–1% Fe–dolomite and 1% Fe–dolomite catalyst for the wash-oil catalytic cracking process in a fixed-bed reactor. It was found that 0.5% Ni–1% Fe–dolomite sample exhibited better catalytic activity in the decomposition of aromatic hydrocarbon than 1% Fe-dolomite catalyst sample. Moreover, the formation of Ni-Fe alloy and NiO phases was detected, which leads to superior stability and prevents carbon deposition on the catalyst. The catalytic cracking of biomass tar to syngas at 750 °C in a fixed-bed reactor was studied by Wang and co-workers.[43] Five different catalysts such as natural dolomite, modified dolomite (mixed with Fe_2O_3 powders), Ni-dolomite (prepared by the incipient wetness method from modified dolomite), ICI-46-1, and Z409 (commercially available nickel-based reforming catalysts) were compared with each other. The Ni-dolomite catalyst exhibited the highest catalytic activity and stability among other studied catalysts in the reaction of biomass tar removal. The tar conversion over this catalyst achieved 97% during 60 h on stream, which was attributed to the high Fe_2O_3 content, moderate pore size distribution, and strong nickel−dolomite interaction.

Precalcined dolomite (CaMg)O, lime (CaO), and magnesia (MgO) impregnated with 20 wt% of iron were synthesized by Di Felice and co-workers[47] for steam reforming of toluene as a model compound of biomass tar in a fixed-bed microreactor. The highest achieved toluene conversion was 70% over Fe-MgO catalyst and decreased to 60% after 6 h on stream. Two impregnation methods were used to generate the Fe^{2+} and Fe^{3+} species, and it was found that both of them, in cooperation with CaO and MgO substrates, are active in the reforming of toluene. Heo et al.[48] investigated the effect of Ca, K, and Mn addition to Ni-based catalyst on different supports (α-alumina, dolomite, and olivine) for toluene steam reforming at 800 °C under steam/carbon (S/C) ratio = 3. It was observed that the use of Ni-Mn-dolomite catalyst resulted in the highest toluene conversion (62.6%), hydrogen formation, and catalyst stability.

Nevertheless, dolomites are rather mechanically fragile and therefore erode quickly because of attrition phenomena in fluidized bed reactors. Another disadvantage lies in rather low catalytic activity for tar conversion in comparison with another type of catalysts.

4.1.2. Olivine. Olivine is a nonporous material that has a low surface area and a negligible pore volume and belongs to a crystalline series of silicates of magnesium and iron ($Mg_2(SiO_4)$ $Fe_2(SiO_4)$).[8] The main advantage of olivine, in comparison to dolomite, is its resistance to attrition because of its high hardness.[9] Price levels of olivine and dolomite are approximately the same. Moreover, some researchers stated that the catalytic activity of olivine can be further improved by the addition of some metals. Virginie et al.[49] found that Fe/olivine material has a double effect on tar destruction which was reduced by up to 65% at 850 °C during biomass gasification in dual fluidized beds. According to Michel and co-workers,[50] Ni/olivine catalyst has a good ability to reform 1-methylnaphthalene (biomass tar model compound) much better than olivine alone. This trend was confirmed by Yang et al.,[51] who used Ni/olivine catalyst calcined at 900 °C and compared with it with conventional Ni/olivine catalyst in the steam reforming of benzene. Higher catalytic activity was exhibited for Ni/olivine, as well as better coke resistance for a modified catalyst. This phenomenon was attributed to the modified pore structure of the olivine and the sufficient Ni−modified olivine interaction. Furthermore, Zhang and co-workers[52] have used 3.0% NiO-olivine, 3.0% NiO-olivine doped with 1.0% CeO_2, and 6.0%NiO-olivine catalysts for tar steam reforming in a bench-scale fixed-bed reactor at 700−830 °C using a molar ratio of S/C equal to 5. It was shown that 3.0%NiO-olivine doped with 1.0% CeO_2 was promising catalyst based on catalytic activity and its resistance to coke formation. Very recently, Meng and co-workers[53,54] found similar trends when studying the steam reforming of phenol and naphthalene as tar model compounds over Ni and Fe olivine-supported catalysts. These catalysts were prepared by thermal fusion (TF) and wetness impregnation (WI) methods. It was reported that Fe-containing catalysts achieved conversion of phenol above 93% and more than 99% with Ni-containing catalysts. The same authors[55] studied TF Fe-olivine catalyst in the steam reforming of toluene at 850 °C. The highest toluene conversion was obtained over Fe-olivine and was near 100% after 48 h on stream, while Fe/Ni-olivine showed the highest resistance to carbon deposition. Moreover, Meng et al.[56] demonstrated high activity of Fe-Ni/olivine catalyst prepared by WI at 1100 °C and TF at 1400 °C for conversion of biomass tar. Fe-Ni/olivine(1100)-WI catalyst achieved of 81.5% tar conversion comparing with 40.6% of raw-olivine. In the case of Fe-Ni/olivine(1400)-TF the conversion of biomass tar was 82.9%. Moreover, the Fe-Ni/olivine(1400)-TF showed higher anti-attrition performance and was more sufficient for the use in a circulating fluidized bed. This catalytic activity was explained by the presence of Fe_2O_3, NiO, and NiO-MgO active centers in the Fe-Ni/olivine(1100)-WI catalyst and $NiFe_2O_4$ formation in the case of Fe-Ni/olivine(1400)-TF catalyst.

The olivine impregnated by 10 or 20 wt% of Fe and calcined at different temperatures from 400 to 1400 °C was studied by Virginie and et al.[57] These synthesized catalysts were tested for toluene reforming in a fixed-bed reactor at 825 °C in the presence of H_2, CO, CO_2, and CH_4. It was demonstrated that toluene conversion was 91% over 10 wt% Fe-olivine catalyst calcined at 1000 °C, which is higher than the conversion of 39% obtained using solely olivine. These results were explained through the high loading of metallic Fe leading to C−C and C−H bonds cleavage and a small quantity of Fe_3O_4 that is the active phase for water−gas shift reaction. Besides this, it was reported that carbon deposits formed from toluene decomposition during the reaction were oxidized by water.

4.2. Synthetic Catalysts. Synthetic catalysts are synthesized by a chemical route and are relatively more costly than the mineral catalysts.[20]

4.2.1. Carbon-Supported Catalysts. Char and activated carbons derived from biomass and coal are becoming interesting as catalyst supports for the cracking of tar due to their highly porous structure and high specific surface area.[1,9,58] The main advantages of char are its low price and its natural production inside the gasifier.[20]

Zhang et al.[59] reported that original biomass char exhibited good catalytic activity in tar cracking and better stability compared to char treated with $Ni(NO_3)_2$. However, biomass char deactivated due to the naphthalene cracking reaction and soot formation on the active sites of the inner microporous surface. The catalytic cracking of biomass tar over 6 wt% Ni-char catalyst was studied by Hu and co-workers[10] in a fixed-bed reactor using steam gasification at 800 °C. Guo et al.[22] worked on catalytic reforming of tar during biomass high-temperature pyrolysis using rice husk char (RHC) and metal-impregnated (Fe, Cu, and K) char in a dual-stage reactor. The authors studied the textural characteristics of synthesized catalysts and found that the addition of Fe and Cu to carbon materials increased the porosity, specific surface area, and total pore volume of the latter. The tar conversions at 800 °C were achieved as follows: RHC, 77.1%; K-RHC, 82.7%; Fe-RHC , 92.6%; and Cu-RHC, 90.6%. Morin and co-authors[60] found that "olivine + 3% char" and "sand + 3% char" catalysts are suitable to limit the amount of tar model compounds (toluene)

DOI: 10.1021/acs.iecr.9b01219
Ind. Eng. Chem. Res. 2019, 58, 7690−7705

Table 2. Conversion of Biomass Tar and Its Model Compounds into Syngas over Noble Metal Catalysts

catalyst						
metal	promoter	support	model compounds	temp (°C)	conversion (%)	refs
Ru	SrO	Al_2O_3	toluene and dodecane	600	56 and 77	70, 71
Rh	$LaCoO_3$	Al_2O_3	biomass tar	700	~100	72
Rh Pt Pd Ru	CeO_2	SiO_2	biomass tar	550−650	64−77 48−76 55−73 45−57	64−66
Pt	–	Al_2O_3	naphthalene and benzene	750−800	≥80	73
Rh	MgO	CeZrO	phenol	350−550	~80	69

during gasification with steam in a fluidized bed reactor and pressure higher than 0.2 bar. Besides this, the catalytic cracking of toluene over sewage sludge char (SSC) was investigated by Lu and co-authors[61] in the temperature range from 750 to 950 °C. Toluene conversions achieved were 65% at 750 °C and 93% at 950 °C, where both CO_2 and steam were fed.

Recently, Xie and co-workers[62] prepared and tested Fe-Ni/carbon nanofibers composite catalyst for the tar conversion during biomass gasification. The tar removal efficiency reached 85.8% and the total syngas yield doubled in comparison with non-catalyst tar conversion. The authors achieved high mesopore volume of the synthesized catalyst due to the formation of carbon nanofibers after calcination, which is beneficial to the adsorption and cracking of macromolecular tar compounds. The catalyst hydrogenation of naphthalene into tetralin was studied by Usman and co-workers[63] over 10 wt% MoP-activated carbon (AC) catalyst at 300 °C under 4.0 MPa. The highest naphthalene conversion and selectivity to tetralin achieved was 82% and 99%, respectively. This reported catalyst activity was related to its moderated acidity and high AC surface area that reduces hydrocracking and increases MoP dispersion, respectively.

The carbon-supported catalysts are deactivated by coke formation, which blocks the pores of the catalysts and reduces the surface area of the latter. Moreover, some of the catalyst is also lost during gasification by the steam and dry reforming reactions.[20]

4.2.2. Noble Metal Catalysts. It is now well known that noble metal catalysts such as Ru, Rh, and Pt (Table 2) have a high catalytic activity with long-term stability and a high sulfur resistance in the steam reforming of tar.[9] Tomishige et al.[64−66] tested M−CeO_2−SiO_2 (M = Rh, Pt, Pd, Ru, Ni) catalysts for the reforming of tars derived from cedar wood, jute, rice straw, and baggase. The results demonstrated that the Rh−CeO_2−SiO_2 catalyst exhibited much higher performance and coke resistance than other catalysts, such as dolomite and commercial Ni-based steam reforming during the reaction of biomass-derived tar reforming. According to Polychronopoulou and co-workers,[67] 0.5 wt% Rh-MgO and 0.1 wt% Rh-Mg-Ce-Zr-O catalysts exhibit better performance when compared to a commercial Ni-based catalyst in the phenol steam-reforming reaction. The same authors[68] further synthesized and tested 0.1 wt% Rh-40Mg-20Ce-20Zr-20La-O catalyst, which exhibited the highest H_2 yield even in comparison to a Ni-based commercial catalyst. Constantinou et al.[69] reported that 0.5 wt% Rh-$Ce_{0.14}Zr_{0.81}Mg_{0.05}O_2$ catalyst exhibited high activity in terms of phenol conversion and H_2 yield, and the lowest CO/CO_2 product ratio in the temperature range 350−550 °C. Moreover, it was revealed that Mg support loading increased the conversion and selectivity toward H_2.

The steam reforming of toluene and dodecane over Ru-12SrO-7Al_2O_3 was studied by Iida and co-workers.[70,71] It was exhibited a high catalytic activity and coking resistance compared to commercial Ru/Al_2O_3 catalyst, despite low Ru loading and dispersion. Ammendola et al.[72] evaluated the effect of H_2S addition on the catalytic activity of Rh-$LaCoO_3$-Al_2O_3 for biomass-derived tar conversion to syngas. It was found that the perovskite layer preserves Rh from poisoning to a large extent. Furusawa and co-workers[73] investigated the influence of support on the catalytic performances of Pt- and Ni-based catalysts for the steam reforming of naphthalene and benzene as model tar compounds of biomass gasification. It was reported that the Pt/Al_2O_3 catalyst has higher and more stable activity compared to the Ni/Al_2O_3 catalyst.

4.2.3. Transition-Metal-Based Catalysts. Transition metals such as Ni, Fe, Co, Cu, Mo, Mn, Mg, Ca, Sr, Ba, and Zn show good activity and are less expensive and sufficiently active in comparison with catalysts based on noble metal such as Pt, Pd, Ru, and Rh for the tar conversion.[9,20,46]

The majority of references have been related to Ni-based catalysts as shown in Table S1 (Supporting Information). Ni-based catalysts can be divided into three main components:

(a) Ni element, where is Ni represents the active site of the catalyst;

(b) Support material, which gives the catalyst mechanical strength and protection against severe conditions such as attrition and heat;

(c) Promoters (alkali and alkaline earth metals) such as Mg (stabilize the Ni crystallite size) and K (neutralize the support surface acidity and thereby reduce coke deposition on the catalyst surface and enhance catalyst activity), which are added to ensure economical operations under severe conditions.[20]

4.2.3.1. Ni-Based Catalysts. Many references[18,40,74−86] pointed out on Ni as a good catalyst for steam reforming of biomass tar or its model compounds. Artetxe et al.[18] studied steam reforming of different biomass tar model compounds such as phenol, toluene, methylnaphthalene, indene, anisole, and furfural and utilized methanol as a solvent to dissolve them. The reaction was carried out over Ni/Al_2O_3 catalysts at 700 °C under a steam/carbon ratio of 3 and 1 h on stream.

The results showed that the highest conversions and H_2 formation were obtained for oxygenated compounds, and specifically for anisole, whereas methylnaphthalene presented the lowest reactivity. The steam reforming of toluene was investigated by Zhao and co-workers[80] over Ni-cordierite catalyst in a fixed-bed reactor at 900 °C. The highest achieved H_2 content was about 66 mol% with the conversion of toluene 94.1%. Benzene and naphthalene were the main products in the aromatic hydrocarbons mixture.

Recently, the steam reforming of toluene and biomass tar over biochar-supported Ni catalysts at 600 °C was reported by Du et al.[79] It was demonstrated that the catalyst with 5% nominal Ni loading and biochar support was the most effective and stable among other Ni-biochar catalysts in the steam reforming of biomass tar. This phenomenon was attributed to the small Ni particle size of this catalyst together with the pyrolysis temperature and Ni loading. The iron-alumina-supported nickel−iron alloy catalysts were tested for steam reforming of toluene in a fixed-bed reactor by Ashok and co-workers.[87] That work showed the influence of calcination temperature on the Fe_2O_3-Al_2O_3 support and established that Ni-Fe_2O_3-Al_2O_3 catalyst calcined at 500 °C achieved a toluene conversion of 90% after 26 h time-on-stream. This activity of Ni-Fe_2O_3-Al_2O_3 catalyst was attributed to the presence of a high catalyst surface area, a higher amount of available lattice oxygen species forming Fe-rich Ni-Fe alloy particles, strong metal−support interactions, and relatively low carbon deposition rate. Later, the same authors[88] carried out the steam reforming of toluene over Ni-supported CaO-Al_2O_3 and CeO_2-promoted CaO-Al_2O_3 catalysts at 650 °C. Ni/Ca-Al-Ce(0.2) catalyst exhibited superior catalytic activity with 70.8% toluene conversion in comparison with other studied catalysts. This behavior was attributed to the presence of Ni-rich surface with a considerably higher amount of Ce species.

The steam reforming of biomass tar and toluene into synthesis gas over Ni-Al_2O_3, Co-Al_2O_3, and Ni-Co-Al_2O_3 was reported by Wang et al.[89] It was shown that catalytic activity, resistance to coke formation, and catalyst life of Ni-Co-Al_2O_3 catalysts were much higher than for the corresponding monometallic Ni and Co catalysts in the steam reforming of biomass tar. The authors explained this phenomenon by the formation of the Ni-Co solid solution alloys. In the case of toluene steam reforming, Co-Al_2O_3 catalyst exhibited higher activity and higher resistance to coke deposition than Ni-Al_2O_3 and Ni-Co-Al_2O_3 catalysts. Oh and co-workers[90] showed that Ni-Ru-Mn-Al_2O_3 catalyst, in reforming of the toluene at 400−800 °C, has high stability and coking resistance that may be related to the promotional effect of Mn addition to the Ni-Ru-Al_2O_3 catalyst. Recently, Savuto et al.[91] used mayenite ($Ca_{12}Al_{14}O_{33}$) as a support and CeO_2 as a promoter for Ni catalyst in the steam reforming of toluene, naphthalene, and thiophene, which were chosen as the tar model compounds. The catalytic test was performed in a fixed-bed stainless steel microreactor at 800 °C. The characterization data of catalyst samples obtained by authors showed that the addition of CeO_2 to Ni-mayenite enhanced the coke resistance and surface area by increasing the porosity. Modification of the Ni species with the mayenite support led to higher reducibility and a higher quantity of the Ni species bonded to free Al_2O_3.

Very recently, the steam reforming of naphthalene over Ni-based catalyst in the presence of HCl was investigated by Veksha and co-workers[92] at 790 °C. The Ni-Al_2O_3 catalyst showed of 100% naphthalene conversion. This behavior was attributed to the enhanced sintering of Ni nanoparticles resulted from the influence of HCl. Furthermore, the same group with Dou et al.[93] found similar trends when studying the poisoning effects of HCl and H_2S on the naphthalene steam reforming over Ni and Fe on Al_2O_3 support catalysts in a fixed-bed reactor at 790, 850, and 900 °C. It was demonstrated that the poisoning of naphthalene reforming activity was affected by H_2S and unaffected when HCl was presented. The highest achieved naphthalene conversion was 100% over Ni-Al_2O_3 and Ni-Fe-Al_2O_3 at 900 °C.

The steam reforming of benzene, toluene, and phenol over Ni-Fe-Mg-Al catalysts was carried out by Koike and co-workers[84] at 600 °C. It was shown that Ni-Fe-Mg-Al (Fe/Ni = 0.25) catalyst showed higher activity, stronger adsorption, and higher coke resistance than Ni-Mg-Al catalyst thanks to the formation of Ni-Fe alloy and highly stable surface carbide on iron. Higo[94] et al. reported that Ba addition has a drastic promoted effect on the catalytic performance of Ni/$LaAlO_3$ perovskite catalyst in the reaction of steam reforming of toluene at 600 °C. This promotional effect of the Ba loading on the steam reforming of toluene was attributed to the enhanced adsorption behavior and the activation of H_2O on the catalyst surface. Very recently, Abbas and co-workers[82] studied the steam reforming of 5 wt% phenol solution over Ni and Co_3O_4 nanocube-supported TiO_2 nanorod (NR) catalysts at 700 °C. The Ni-Co_3O_4-TiO_2 NR catalyst exhibited high stability even after 100 h what was attributed to nanocubes heterojunction, high metal dispersion, and higher reducibility, thus providing a strong interaction of bimetallic active sites. Finally, Rached et al.[95] reported steam reforming of toluene over $Ni_xMg_{6-x}Al_{1.8}Ce_{0.2}$ (with $0 \leq x \leq 6$) mixed oxide catalysts. These catalysts were prepared by the hydrotalcite route and calcined at 800 °C. The authors declared that the $Ni_2Mg_4Al_{1.8}Ce_{0.2}$ catalyst resulted in total (100%) toluene conversion and the best performance among other synthesized and studied catalysts.

However, it has been reported[25,65,69] that the Ni-based catalysts were deactivated significantly by carbon deposition on the catalyst surface and poisoning of Ni sites due to the presence of H_2S. Besides Ni catalysts, other metals like Fe, Co, Cu, Mo, Mn, Mg, Ca, Sr, Ba, and Zn have also been investigated in the conversion of biomass tar or its model compounds, and some of them, like Fe and Ca, showed higher catalytic activity compared to Ni (Table S1).

4.2.3.2. Fe-Based Catalysts. It is well-known that the catalytic activity of iron depends on its oxidation states such as Fe_2O_3, Fe_3O_4, or Fe^0.[25] Azhar Uddin and co-authors[96] studied the decomposition of biomass tar over Fe_2O_3 catalysts. The key factor for the catalytic removal of tar was the surface area of Fe_2O_3. It was shown that the addition of Al_2O_3 to Fe_2O_3 increased the surface area without its deactivation. The highest achieved tar conversion was 90% at 850 °C. The steam reforming of naphthalene as a model compound of biomass tar over Fe-Al and Fe-Zr with the addition of CuO at 850 °C in a fixed-bed reactor was reported by Noichi and co-workers.[97] It was established that the catalytic activities for naphthalene conversion increased with higher Fe loading. Moreover, upon addition of CuO to Fe-Al catalyst, the activity and stability of the latter were increased. This behavior was explained by authors as a result of high copper dispersion in the compound oxides, which facilitated the reduction of iron oxides to metallic iron and prevented catalytic deactivation due to a decrease in the surface area of the catalysts during the reaction. The steam reforming of naphthalene with syngas mixtures and H_2S over rare earth oxides (REOs) mixed with transition metals was reported by Li et al.[98] It was found that Fe- and Mn-doped supported REOs are promising tar removal catalysts with higher sulfur tolerance, less coking, and less methanation than conventional Ni-based high-temperature reforming catalysts in the temperature range of 650−800 °C. This phenomenon was related to the increased generation of oxygen vacancies in the metal-doped REOs. Finally, Adnan and co-workers[99,100] reported that Fe_2O_3-SiO_2-Al_2O_3 and Fe-Co-Ce-ZrO_2 catalysts are promising fluidized-bed catalysts for catalytic steam reforming of toluene. It was demonstrated that Fe_2O_3-SiO_2-Al_2O_3 showed a promising 76% toluene conversion at 600 °C as well as a great potential for industrial application due to its a relatively cheap, nontoxic, and long-lasting operation. At the same time, the Fe-Co-Ce-ZrO_2 catalyst showed better performance among other synthesized catalysts for the long-term operation, with the highest H_2 yield of 63% at 700 °C.

4.2.3.3. Ca-Based Catalysts. It is known that CaO is the most commonly used basic catalyst for tar reforming. Indeed, according to Widyawati et al.,[101] CaO can improve the tar cracking and char decomposition during the pyrolysis of cellulose, xylan, lignin, and pine wood. This trend was confirmed by Jordan and co-workers,[102] who studied the effect of CaO on tar production during gasification of fuel cane bagasse in a novel downdraft gasifier. At the same time, CaO particles tend to agglomerate and can be evacuated by the stream. However, the addition of CaO to γ-Al_2O_3 allows retaining a high dispersion of CaO particles and provides a synergetic effect between CaO and γ-Al_2O_3.[25] Recently, a novel CaO-based sorbent (Ca-Fe-Al) was developed, consisting of CaO, Fe_2O_3, and mayenite for reforming of biomass tar by Han and co-authors.[103] Thereafter, Yin et al.[104] investigated the steam reforming of toluene over natural calcium-rich minerals and a novel dual-supported CaO-$Ca_{12}Al_{14}O_{33}$/Al_2O_3 catalyst in the temperature range from 600 to 800 °C. This catalyst demonstrated better performance other studied catalysts with the highest toluene conversion of 73% at 800 °C. Promising results were ascribed to (i) the mayenite support structure that increased the reactivity of CaO when utilized together, (ii) superior surface area, and (iii) mechanical strength of the catalyst.

All transition metals considered above can significantly reduce tar or its model compounds, but they have also some disadvantages like higher price than a conventional nickel catalyst and high deactivation rate due to carbon deposition.

4.2.4. Alkali Metal Catalysts. The alkali metals are group 1A in the periodic table, consisting of chemical elements including Li, Na, K, Rb, and Cs. Many literature data proved that alkali metal catalysts have the high-efficiency in steam reforming of tar and can improve the quality of gaseous products.[2,9,105−109] According to Mitsuoka et al.,[106] K and Ca compounds supported on char exhibited an enhanced catalytic effect during CO_2 gasification at 850−950 °C. These trends were also confirmed by Kuchonthara and co-workers,[107] who demonstrated that tar can be decomposed by adding K_2CO_3 during pyrolysis and steam gasification of lignin at 800 °C. According to Yuan et al.,[109] sodium titanate catalysts degrade biomass tar to hydrogen through cracking, water−gas shift, and/or methane reforming at 850 °C. The $4Na_2O \cdot 5TiO_2$ catalyst exhibited the highest activity, with tar conversion of 99% after 8 h time-on-stream; at the same time, the $Na_2O \cdot 3TiO_2$ catalyst showed the best stability.

It is well-known that alkali species in biomass have a catalytic role in the thermal cracking reactions. The released alkali species in ashes can also act as catalysts for tar steam reforming.[2,9,20] The use of ashes as catalysts has some advantages, such as avoiding the problem of the handling of ash wastes and increasing the gasification rate and reducing the tar content in the produced gas.[2,9,20] Recently, Guo and co-workers[110,111] studied the primary tar vapor from biomass at 700 °C over PSA (high ash-containing paper sludge ash), CaO, Fe_2O_3, and CaO/Fe_2O_3 catalysts with achieved tar conversion of 62.8%, 73.8%, 63.7%, and 68.9%, respectively. The authors concluded that the catalytic performance of the PSA is comparable to the pure metal oxides.

The major disadvantages of the alkali metal catalysts are their evaporation during the reaction, difficult recovery, and easy deactivation as a result of sintering at high temperatures.[2,9,112] The ash-borne catalysts lose their activity due to particle agglomeration.[2]

4.2.5. Zeolite Catalysts. Zeolites (crystalline silicates and aluminosilicates linked through oxygen atoms) are solid acid catalysts with unique combinations of properties such as high surface area, high thermal stability, high adsorption capacity, molecular dimensions of the pores, partitioning of reactant/products, possibility of modulating the electronic properties of the active sites, possibility for preactivating the molecules by strong electric fields and molecular confinement, and ability to confine active metal species.[9,105,113]

Zeolites are environmentally friendly catalysts, largely used in industry for catalytic cracking, alkylations, skeletal isomerizations, etc.[114] The main key parameters of zeolites are acidity and basicity, structure, SiO_2/Al_2O_3 ratio, particle size, and nature of the exchanged cation.[20,105,114] These factors influence on catalytic activity and thermal stability of zeolite catalysts. Zeolites are inexpensive catalysts, which is the main advantage, while these catalysts have rapid deactivation rate due to coke formation what is the main disadvantage.[20]

In previous papers, the authors[24,34,115] concluded that different types of zeolites such as HZSM-5, HY, Mordenite, Beta, Al-MCM-41, HUSY, SBA-15, and Al-MSU are prospective catalysts for the conversion of biomass tar into useful chemicals. The reactions of deoxygenation, aromatization, cracking, isomerization, cyclization, and polymerization occur throughout the whole process as the main thermocatalytic reactions over zeolite catalysts.[115] Table S2 (Supporting Information) shows the summary of these results. Mihalcik et al.[116] reported that HZSM-5 zeolite catalyst is the most effective for yielding aromatic hydrocarbons from the pyrolytic vapors in comparison with zeolite Y, Beta, Mordenite, and Ferrierite. At the same time, the authors proved that the SiO_2/Al_2O_3 ratio of zeolite catalysts is important in the deoxygenation of the vapors through the pathway to aromatic hydrocarbons. Bi and co-workers[34] used HZSM-5, HY, and MCM-41 zeolite catalysts for the transformation of biomass tar to BTX aromatics mixture through current-enhanced catalytic conversion at 400 °C in atmospheric pressure. It was demonstrated that HZSM-5 zeolite catalyst has better catalytic activity with the selectivity of 92.9 mol% and 25.1 wt% yield. This enhanced activity was attributed to the differences in acidity and topology of reported zeolites. Besides this, the authors established the synergistic effect between zeolite catalyst, which appeared to promote the deoxygenation and cracking reactions, despite the still low yield of BTX aromatics. Laksmono et al.[117] investigated the valorization of tar into fuel

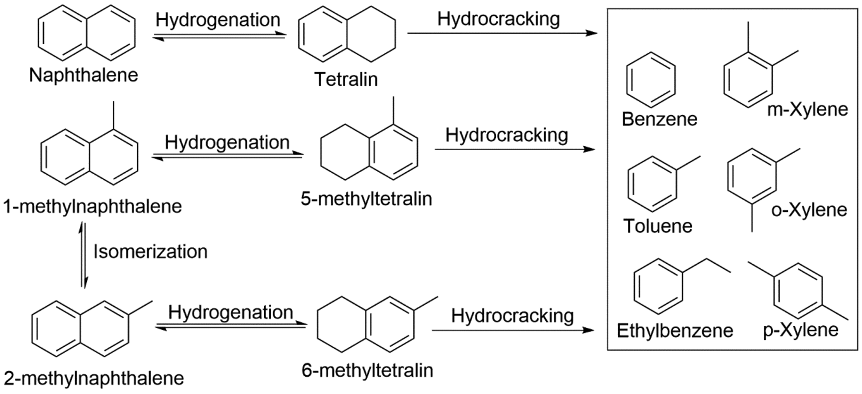


Figure 6. Catalytic hydrocracking reaction pathway for the upgrading of PHAs, represented by naphthalene and 1-methylnaphthalene as model compounds, into value-added BTX mixture. Adapted from refs 120 and 124−128.

for internal combustion engine over HZSM-5, MgO, and Al_2O_3 catalysts and achieved yields of biodiesel of 62−75, 55−66, and 67−71 wt%, respectively. Dou and co-workers[118] found that the Y-zeolite and Ni-Mo catalysts are effective catalysts and removed 100% of the tar component at 550 °C, where 1-methylnaphthalene was chosen as a model compound of biomass tar. The results showed that the temperature and space velocity have very significant effects on conversion of tar over all studied catalysts.

Thus, among all presented catalysts for the reaction of biomass tar conversion into BTX, the H-ZSM-5 zeolite in tandem with current (synergistic effect) is the most prospective catalyst with obtained BTX aromatics selectivity of 92.9 mol% and 25.1 wt% of yield at 400 °C. At the same time the deactivation of the considered zeolite catalysts was observed, due to coke formation and compounds that react with the acidic sites. It was observed[20] that coke decreases of the surface area and zeolite micropore volume by blocking its channels. Furthermore, steam, basic nitrogen compounds, and alkaline metals react with the catalyst acidic sites and deactivate them.

4.2.6. Metal-Promoted Zeolite Catalysts. It is elucidated that the crystalline structures of the zeolites with coordinated Si, Al, or P as well as transition metals and many group elements such as B, Ga, Fe, Cr, Ge, Ti, V, Mn, Co, Zn, Be, Cu, etc. can be synthesized.[119] Bifunctional zeolite catalysts with metal species on acid zeolite-support with hydrogenation−dehydrogenation functions are frequently used.[120] The modification of zeolites with dispersed metallic species showed a relatively high tolerance for sulfuric compounds and suitability for hydrogenation and ring-breaking reactions of aromatic hydrocarbons.[9,105] Some transition-metal-containing zeolites are utilized as redox catalysts, such as for catalytic reduction (SRD) of NOx with ammonia and abatement of N_2O by activation and reduction with methane.[2,114] Moreover, the metal-promoted zeolite catalysts have been applied for the partial and deep oxidation of hydrocarbons, which exhibited that transition metal cations enhanced zeolites' activity for hydrocarbon conversion by increasing the zeolite acidity and oxygen chemisorption capacity. In addition, the alkali- and alkali-earth-promoted zeolites are largely utilized as industrial adsorbents for gas purification, including CO_2 capture, to produce membranes for gas separations and as ion exchangers for water softening.[2,114]

4.2.6.1. Conversion of Biomass Tar. In the case of biomass-derived tar catalytic cracking, various kinds of metal-promoted zeolites were tested by many researchers and summarized in Table S2. According to Chen et al.,[24] HZSM-5 (SiO_2/Al_2O_3 = 50) zeolite with Ni and Ni-MgO metals loading exhibited remarkable catalytic cracking activity. It was concluded that when the loadings of Ni and MgO were 6 and 2 wt%, respectively, the tar conversion reached 91%, and the catalytic activity of Ni-MgO-ZSM-5 catalyst was higher than for Ni-ZSM-5. Moreover, it was shown that with the addition of MgO to Ni-ZSM-5 catalyst, the acidity of catalysts became weaker and also the coke deposition decreased to 11.7 wt%. Recently, the same authors[121] studied the low-temperature catalytic cracking of biomass tar over Ni-ZSM-5. This zeolite catalyst with 6 wt% of Ni loading showed 91.5 wt% of tar conversion, 6.40 MJ/Nm^3 of the heat value of gaseous products and 0.65 h^{-1} of WHSV at 500 °C. However, the carbon yield of reported catalyst was higher than 19.2 wt%. Kaewpanha and co-workers[122] synthesized by the incipient wetness impregnation method Ni-, Fe-, and Rh-X-type zeolite catalysts and tested them in the steam reforming of biomass tar in a fixed-bed reactor at 610 °C and atmospheric pressure. The authors concluded that the Rh-X zeolite catalyst exhibited the highest catalytic activity among all prepared catalysts in the reaction of the tar removal due to higher dispersion of the active metal on the surface of zeolite beads.

4.2.6.2. Conversion of Naphthalene. Selective hydrogenation and hydrocracking are common ring-opening reactions used for effective conversion of the biomass tar model compounds, for instance, bicyclic aromatics such as naphthalene and/or 1-methylnaphthalene hydrocarbons to monocyclic aromatics such as benzene, toluene, ethylbenzene, and xylene (BTEX).[123] Figure 6 shows the catalytic hydrocracking reaction pathway of naphthalene and 1-methylnaphthalene to BTX aromatics mixture. It is well-known that naphthalene is the most common compound in PAHs and is first hydrogenated into tetralin, and then tetralin is hydrocracked to yield BTX.[124] Therefore, the hydrocracking of tetralin into BTX presented in Figure 6 also can be selected as a representative model reaction to study hydrocracking catalysts and compare their performance.

The main findings regarding naphthalene conversion to BTX mixture, syngas, or tetralin are shown in Table S2. The hydrocracking of 5 wt% naphthalene in tridecane solvent over Ni_2P catalysts supported on ZSM-5, Beta, and USY zeolites by temperature-programmed reduction was studied by Kim and co-workers.[129] The reaction was carried out in a three-phase fixed-bed reactor with the highest naphthalene conversion of

99% and a BTX yield of 94.4% at 400 °C and 3.0 MPa. This catalyst performance was explained by unique catalytic nature of the synthesized catalysts through the moderate acidity and porosity combined with hydrogenation activity of well-dispersed Ni_2P phase. Nevertheless, this marvelous BTX yield did not include the gas fraction from the cracking of naphthalene and tridecane, that can significantly reduce its value.[120]

Buchireddy et al.[130] studied the reduction of naphthalene to syngas over various zeolites such as HY(5.2; 30; 80), HZSM-5(24), Hβ(25), and Ni-promoted zeolites, where the number in parentheses is the SiO_2/Al_2O_3 ratio. The catalytic results indicate that Ni-Y catalysts with SiO_2/Al_2O_3 = 30 and 80 have the highest naphthalene conversion of more than 99% and stability for 97 h on stream compared with other studied catalysts. This high activity of Ni-promoted zeolite Y catalyst was attributed to the nickel species activity and the zeolite acid nature.

Usman and co-authors[131] synthesized MoP catalyst supported on HZSM-5, Hβ, and HY by wet impregnation and H_2-TPR for the selective conversion of 10 wt% naphthalene (dissolved in *n*-heptane solvent) into tetralin. The catalysts evaluation was carried out using a fixed-bed reactor at 300 °C, LHSV of 3 h^{-1}, and a hydrogen pressure of 4.0 MPa. MoP-HY catalyst exhibited the highest conversion of 85% and selectivity of 99% in comparison with other zeolite supports for the formation of tetralin from naphthalene. It was established that the MoP-HY catalyst showed the high catalytic activity due to the lowest pore volume, high dispersion, small metal particles, and weak acid sites of the HY zeolite support in comparison to HZSM-5 and Hβ.

Choi and co-workers[126] investigated hydrocracking of 5 wt% naphthalene or 1-methylnaphthalene (dissolved in *n*-heptane) into tetralin and subsequent hydrocracking of the latter into BTX over Hβ and Ni-β zeolite catalysts in a down-flow fixed-bed reactor at 3−4 MPa. The bifunctional Ni-β demonstrated the BTX selectivity in liquid product of 69.5% and the total BTX yield of 40.7 wt%, at the same time the tetralin conversion was 99.5% at 450 °C under 4 MPa. It was reported that high catalytic performance was achieved due to hydrogenation activity of metallic sites, the acidity of Hβ zeolite support, and their balance within a bifunctional catalyst.

The hydrogenation and the ring-opening reactions of naphthalene, tetralin, and decalin over Mo_2C-HY, Mg-Mo_2C-HY, K-Mo_2C-HY, and Pd-HY catalysts were studied by Ardakani and co-workers[132] at 300 °C under 3 MPa. It was demonstrated that, with the addition of Mg or K to Mo_2C-HY catalyst, the conversion of naphthalene, tetralin, or decalin decreased, as did the carbon deposition. The hydrogenation of naphthalene to tetralin over Mo_2C-HY catalyst with the addition of Mg (0.5−2 wt%) and K (1 wt%) was studied by the same group with Liu and co-authors.[133] It was concluded that catalyst acidity and metal dispersion are the key parameters that influence catalyst activity. With the addition of K and Mg, the dispersion of Mo_2C was improved, but not even a moderate acidity was achieved. The main product obtained after naphthalene hydrogenation reaction over 20% Mo_2C-HY and 1.0% K-20% Mo_2C-HY was tetralin, with relatively small differences in selectivity (81%, 84%) and conversion (95%, 94%), respectively.

After the comparison catalytic performance for naphthalene conversion, it can be concluded that the most suitable catalyst for BTX formation considering both yield and selectivity is the Ni_2P-β catalyst.

4.2.6.3. Conversion of 1-Methylnaphthalene.

Recently, Kim et al.[134] synthesized Ni_2P-β-nanometer-sized and Ni_2P-β-micrometer-sized catalysts and tested them in the hydrocracking reaction of 1-methylnaphthalene with 15 wt% of phenanthrene to BTX at 380 °C and 6.0 MPa in a fixed-bed reactor. Ni_2P-β-nanosized catalyst exhibited higher yield than Ni_2P-β-micrometer-sized catalyst in the reaction of 1-methylnaphthalene hydrocracking to BTX with obtained yields of 42.3% and 30.5%, respectively. The characterization data showed that the β-nanosized zeolite has higher activity in the PAHs hydrocracking due to the abundant intercrystalline mesopores, resulting in better dispersion of Ni_2P and accessibility to acidic sites. The conversion of 1-methylnaphthalene was described by the parallel reaction network, where each single reaction is irreversible and follows pseudo-first-order kinetics. It was shown that the obtained experimental results were correlated with the pseudo-first-order reaction rates. Park and co-authors[127] reported the hydrocracking of 10 wt% solution of 1-methylnaphthalene in dodecane to (alkyl)-benzenes and BTX mixture over NiMoS supported on USY-alumina zeolite and USY zeolite coated with alumina. The reaction was carried out at 360−400 °C for 6 h under 5 MPa. The catalytic results indicate that NiMoS alumina-coated USY zeolite catalyst has higher coke resistance and activity than catalysts supported on alumina-USY with an obtained yield of 80.5%. This can be explained by a strong surface acidity of USY being exposed to the substrate.

Recently, the hydrocracking of 1-methylnaphthalene to BTX aromatics over a series of sulfided M-β catalysts (where is M = NiMo, NiW, CoMo, CoW, Mo, W) was studied by Wu et al.[123] The reaction was carried out at 420 °C under 6 MPa. It was revealed that 25 wt% W-β catalyst with SiO_2/Al_2O_3 ratio of 30 is the best among all prepared catalysts, and a BTX yield of 53 wt% was obtained. These results were explained by the relatively highly selective hydrogenation activity of W and suitable metal−zeolite interactions. The hydrogenation and hydrocracking of 1-methylnaphthalene (10 wt%) with dibenzothiophene (0.1 wt%) in decalin solvent to BTX mixture were tested by Ishihara and co-authors[135] over zeolite−alumina composites such as β, Y, USY, and ZSM-5-supported NiMo at 360 °C under 5 MPa. The NiMo-β catalyst with SiO_2/Al_2O_3 ratio of 37 showed high hydrocracking activity and yields of BTX aromatics with the 1-methylnaphthalene conversion of 96%. The catalyst characterization results revealed that pore sizes in mesoscale are important for hydrocracking as well as the acid sites' strength and homogeneous metal dispersion.

Lee et al.[136] synthesized NiW catalyst supported on Beta zeolite with different silylation agents such as tetramethyl orthosilicate, tetraethyl orthosilicate, and tetrabutyl orthosilicate (TBOS). It was exhibited that NiW-TBOS-silylated Beta zeolite catalyst has the best catalytic activity in the selective ring opening reaction of 1-methylnaphthalene with the ring opening yield of 58.5% at the conversion more than 97.0%. The reaction was carried out in a fixed-bed reactor at 400 °C under pressure of 5 MPa. This catalyst activity was explained as the optimal balance of metallic and acidic functions of the NiW-TBOS-silylated Beta zeolite catalyst. The same authors[137] recently reported that the NiW-loaded Beta zeolite catalysts with various Ni contents has good catalytic performance in the reaction of selective ring opening of 1-methylnaphthalene to

BTEX. The $Ni_{1.1}W$-Beta catalyst showed the best catalytic performance among other studied catalysts with BTEX yield of 39.6%. This achieved performance also was related to the optimal balance of metallic and acidic functions of the synthesized catalyst.

The catalytic activity of several catalysts tested in 1-methylnaphthalene conversion into BTX is presented in Table S2. It can be concluded that 25%W-β catalyst synthesized by Wu and co-workers[123] exhibited the best performance in terms of 1-methylnaphthalene conversion and catalyst stability.

4.2.6.4. Conversion of Tetralin. Shin et al.[125] studied hydrocracking of tetralin model compound into BTX over Ni, NiSn, CoMoS, NiMoS, and NiWS with Hβ supports and hybrid zeolites (a physical mixture of Hβ and HZSM-5) at 425 °C. Enhanced catalytic activity was reported for the hydrocracking of PAHs into BTX mixtures over NiMo-S-HZSM-5(10 wt%)-Hβ catalyst with BTX yield of 54.3 wt%. This catalytic behavior was attributed to a sufficient balance between acidic functions and structural properties of the zeolite catalyst.

Upare and co-workers[138] prepared Mo and CoMo catalysts on different supports such as β-zeolite (SiO_2/Al_2O_3 = 25, 75, 150), mordenite (SiO_2/Al_2O_3 = 20), amorphous silica–alumina (SiO_2/Al_2O_3 = 20), and activated carbon (20–40 mesh size). The catalyst samples were prepared by the wet-impregnation method for hydrocracking reaction of tetralin and pyrolysis fuel oil into BTX aromatics mixture at 370 °C under 8 MPa. The catalytic results exhibited that Co introduced to Mo-β catalyst with SiO_2/Al_2O_3 = 25 improved the catalytic activity and stability in the hydrocracking reaction. In the formation of BTX aromatics from tetralin and pyrolysis fuel oil, the achieved product yields were 54.2% and 31.3%, respectively. The respective conversions of tetralin obtained from bimetallic CoMo-β zeolite were 99.5% and 70% in the case of conversion of pyrolysis fuel oil. This phenomenon of synthesized bimetallic catalyst was explained as a synergetic effect between Co and Mo with moderate acidity in β zeolite support.

The hydrocracking of tetralin into BTX aromatics mixture was studied by Lee and co-authors[124] over Ni, Ni-Sn, and CoMo-S on Hβ zeolite support at 375–450 °C under 4 MPa. NiSn-β catalyst exhibited the highest BTX yield of 48.1 wt% in comparison with Ni-β zeolite catalyst due to suppressing of Ni activity through the forming Ni-Sn intermetallic compounds. The BTX yield corresponded to 47.4 wt% was achieved over CoMo-S-β catalyst. It was shown that, besides metallic function in hydrocracking catalyst, H_2/tetralin molar ratio higher than 4 and zeolite support catalyst with a moderate acidity are important for effective hydrocracking of tetralin into BTX with high selectivity.

A catalyst comparison in terms of activity for the tetralin conversion at various operating conditions is summarized in Table S2. It can concluded that NiMo-S-HZSM-5(10 wt %)-Hβ and CoMo-β catalysts both exhibit superior and comparable results.

4.2.6.5. Conversion of Other Model Compounds. Very recently, Ahmed and co-authors[139] investigated the steam reforming of toluene as a biomass tar model compound over Ni-Fe-Mg zeolite supported catalysts. The authors established that addition of Mg to Ni-Fe-zeolite catalyst enhanced the tar reforming reactions and increased the carbon deposition resistance. The steam reforming of toluene over 5 wt% Ni-SBA-15 with the addition of La_2O_3 promoter was studied by Oemar and co-workers[140] in a quartz tube fixed-bed micro-catalytic reactor at 700 °C. 1%La5%Ni-SBA-15 catalyst showed the highest activity and stability in toluene reforming with conversion above than 95%. This phenomenon was attributed to La-doping which is removed the deposited carbon by the formation of oxycarbonate. Lee et al.[141] investigated the selective ring-opening of phenanthrene into BTEX (BTX involving ethylbenzene) aromatics mixture over NiW-supported mesoporous HY zeolite catalyst in a batch reactor at 375 °C under 10 MPa. The presence of mesopores in HY zeolite enhanced the yield of BTEX aromatics to 48.4% at 99.9% conversion due to lower internal mass transfer resistance.

5. CONCLUSIONS

The purpose of this Review is to provide an systematic overview of various types of catalysts that have been used in cracking of biomass tar or its model compounds into BTX aromatics. It was demonstrated that the key issue for the successful biomass tar process is the catalyst design.

The advantages and disadvantages of the different types of catalysts are summarized below:

(1) Natural catalysts have been widely applied for the steam reforming of tar since they are inexpensive, abundant, and disposable, but their catalytic activities are lower than those of the synthesized catalysts, and they have especially low mechanical strength, hindering their use in fluidized-bed reactors.

(2) Carbon-supported catalysts have low price, and their natural formation inside the gasifier is advantageous, but on the other hand they are rapidly deactivated by coke formation, which blocks the pores of the catalyst and reduces the surface area. Loss of catalysts due to the gasification of the latter by steam and dry reforming reactions has to be taken into account.

(3) Noble-metal-based catalysts have high catalytic activity, long-term stability, and high carbon deposition resistance, but they are expensive to use in a large-scale biomass tar conversion process.

(4) Alkali metal catalysts also have high catalytic activity for tar reforming, but they are easily evaporated with the generated gases, are difficult to recover, and tend to deactivate as a result of sintering at high temperatures.

(5) Transition metal catalysts such as Ni, Fe, and Ca exhibited promising performance, but they are easily deactivated by coking in the case of high heavy-tar content.

(6) Zeolites such as HZSM-5, HY, Mordenite, Beta, Al-MCM-41, HUSY, SBA-15, and Al-MSU are reported to be suitable catalyst supports due to their high thermal/hydrothermal stability, high resistance to sulfur compounds, and easy ability to regenerate.

(7) Metal-promoted zeolite catalysts are reported to be the superior class catalysts due to their higher activity compared to pure zeolites, while retaining the thermal stability, sulfur and coke compounds resistance, and simplicity of regeneration.

Thus, this Review summarizes the basics and the most recent progress applied to catalytic cracking of biomass tar or its model compounds to BTX and other useful products. The most promising catalysts for this purpose are the metal-promoted zeolite catalysts but their development, improvement, and optimization are still necessary. In the case that catalyst issues (listed above) are adequately solved in the near future, the effective utilization of biomass tar is expected to be implemented, which will allow the use of commodity products produced from biomass-derived chemicals even more often in our everyday life.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.iecr.9b01219.

> Reforming of biomass tar and its model compounds over transition-metal-based catalysts (Table S1); conversion of biomass tar and its model compounds over zeolite and metal-promoted zeolite catalysts (Table S2) (PDF)

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ACKNOWLEDGMENTS

The authors acknowledge financial support from the EU Framework Programme for Research and Innovation Horizon 2020 under Grant Agreement No. 818135 (CONVERGE) and from the Slovenian Research Agency (research core funding No. P2-0152). The work was partially carried out within the RDI project Cel. Cycle: "Potential of biomass for development of advanced materials and biobased products", which is co-financed by the Republic of Slovenia, Ministry of Education, Science and Sport, and the European Union through the European Regional Development Fund, 2016−2020.

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