

Milestone Report

A Review of the Literature on Catalytic Biomass Tar Destruction

Milestone Completion Report

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EXECUTIVE SUMMARY

The objective of this report is to summarize the literature pertaining to catalytic biomass gasification “tar”^{*} destruction, provide an overview of the different catalysts that have been studied and how they have been implemented, and evaluate the future potential of this gas cleaning technology.

Calcined dolomites are the most widely used nonmetallic catalysts for tar conversion in biomass gasification processes. They are relatively inexpensive and are considered disposable; however, they are not very robust and quickly undergo attrition in fluidized bed reactors. Consequently, dolomites find most use in fixed bed catalytic reactors. Tar conversion efficiency is high when calcined dolomites are operated at high temperatures (900°C) with steam. Olivine, another naturally occurring mineral has also demonstrated tar conversion activity similar to that of calcined dolomite. Olivine is a much more robust material than calcined dolomite and has been applied as a primary catalyst to reduce the output tar levels from fluidized bed biomass gasifiers.

Commercial Ni catalysts are designed for use in fixed bed applications and are not robust enough for fluidized bed applications, therefore are not useful as primary, in-bed catalysts. These catalysts, however, have been extensively used for biomass gasification tar conversion as secondary catalysts in separate fixed bed reactors operated independently to optimize performance. They have high tar destruction activity with the added advantages of completely reforming methane and water-gas shift activity that allows the H₂:CO ratio of the product gas to be adjusted. Some studies have also shown that nickel catalyzes the reverse ammonia reaction thus reducing the amount of NH₃ in gasification product gas.

A limitation of nickel catalyst use for hot gas conditioning of biomass gasification product gases is rapid deactivation, which leads to limited catalyst lifetimes. Ni catalyst deactivation is caused by several factors. Sulfur, chlorine, and alkali metals that may be present in gasification product gases act as catalyst poisons. Coke formation on the catalyst surface can be substantial when tar levels in product gases are high. Coke can be removed by regenerating the catalyst; however, repeated high temperature processing of nickel catalysts can lead to sintering, phase transformations, and volatilization of the nickel. Continued disposal of spent toxic Ni catalysts is not economical and poses an environmental hazard.

Using fixed dolomite guard beds to lower the input tar concentration can extend Ni catalyst lifetimes. Adding various promoters and support modifiers has been demonstrated to improve catalyst lifetime by reducing catalyst deactivation by coke formation, sulfur and chlorine poisoning, and sintering. Several novel, Ni-based catalyst formulations have been developed that show excellent tar reforming activity, improved mechanical properties for fluidized bed applications, and enhanced lifetimes. Several of these proprietary research catalysts warrant additional investigation for specific individual gasification processes.

A critical gap identified for catalytic tar reforming technology in biomass gasification processes is the need for extended lifetime studies of promising commercial or novel catalysts. Catalytic hot gas conditioning will not become a commercial technology unless adequate catalyst lifetimes can be demonstrated, even for inexpensive, disposable catalysts like calcined dolomite. Assessment of catalyst lifetimes will allow biomass gasification developers to accurately evaluate the cost of this unit operation. The effects of catalyst poisons like sulfur, chlorine, and alkali metals and continued catalyst regeneration can be critically evaluated with long term catalyst testing. Understanding these issues will enable the

^{*} The term “tar” still lacks a broadly accepted definition in the field of biomass gasification. In the context of this report it is taken to mean all aromatic hydrocarbons with a molecular weight of 78 (benzene) or higher. The reader is referred to [Milne, Abatzoglou, and Evans, (1998) and Neeft, et al. (1999)] for a thorough discussion of this topic.

proper selection of gas conditioning technology matched to the desired end-use application of the biomass gasification product gas. Accurate catalyst cost and lifetime figures will provide important input for techno-economic analyses of developing gasification technologies.

Hot gas conditioning using current or future commercially available catalysts offers the best solution for mitigating biomass gasification tars. Tars are eliminated, methane can be reformed if desired, and the H₂:CO ratio can be adjusted in a single step. The best currently available tar reforming process consists of a calcined dolomite guard bed followed by a fixed bed Ni catalyst reforming reactor operating at about 800°C. Selection of the ideal Ni catalyst is somewhat premature. Commercially available steam reforming catalysts have been demonstrated; however, several of the novel research catalysts appear to have the potential of longer lifetimes that should be verified. This dual bed hot gas conditioning concept has been demonstrated and can be used to condition the product gas from any developing gasification process. For fluidized bed gasifiers, the guard bed could potentially be eliminated if olivine is used as the bed material. A proprietary Ni monolith catalyst has also shown considerable promise for biomass gasification tar destruction and also warrants future consideration.

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INTRODUCTION

Biomass thermochemical conversion for the production of fuels, chemicals, and combined heat and power has a number of realizable social, political, and economic benefits. In the biorefinery concept, it is possible to utilize biomass to generate a number of product and revenue streams that could revitalize rural economies, increase national security by reducing the dependence on foreign oil imports, and improve the global environment by reducing fossil fuel emissions, including greenhouse gases and oxides of nitrogen and sulfur. Biomass gasification is a developing technology that can be used to achieve an increased use of biomass by generating a product gas rich in H_2 and CO . Integrated biomass gasification combined-cycles can then be used to generate electricity in a gas turbine or a fuel cell at higher efficiencies than direct biomass combustion. Conditioning and upgrading the biomass gasification product gas can make it a suitable feed for methanol or Fischer-Tropsch liquid synthesis. Additional conditioning can produce an essentially pure hydrogen product gas for transportation, chemical production, or electricity generation in fuel cells.

The product gas formed from biomass gasification contains the major components CO , H_2 , CO_2 , CH_4 , H_2O , and N_2 , in addition to organic (tars) and inorganic (H_2S , HCl , NH_3 , alkali metals) impurities and particulates. The organic impurities range from low molecular weight hydrocarbons to high molecular weight polynuclear aromatic hydrocarbons. The lower molecular weight hydrocarbons can be used as fuel in gas turbine or engine applications, but are undesirable products in fuel cell applications and methanol synthesis. The higher molecular weight hydrocarbons are collectively known as “tar.”

One of the issues associated with biomass gasifier tars is how they are defined. More often than not, tar is given an operational definition by those conducting biomass gasification R&D. An excellent report by Milne, Abatzoglou, and Evans (1998) describes in detail the operational definitions of biomass gasification tars as published in the literature and provides a comprehensive survey of tar formation and conversion. It is not the intent of this report to provide the definition of “tars” but, for the most part, “tars” are considered to be the condensable fraction of the organic gasification products and are largely aromatic hydrocarbons, including benzene. The diversity in the operational definitions of “tars” usually comes from the variable product gas compositions required for a particular end-use application and how the “tars” are collected and analyzed. Tar sampling protocols are being developed [Simell, et al. (2000) and Neeft, et al. (1999)] to help standardize the way tars are collected; however, these methods are not yet widely established. Regardless of how “tar” is defined, tar removal, conversion, or destruction is seen as one of the greatest technical challenges to overcome for the successful development of commercial advanced gasification technologies.

Tars are problematic in integrated biomass gasification systems for a number of reasons. Tars can condense in exit pipes and on particulate filters leading to blockages and clogged filters. Tars also have varied impacts on other downstream processes. Tars can clog fuel lines and injectors in internal combustion engines. Luminous combustion and erosion from soot formation can occur in pressurized combined-cycle systems where the product gases are burned in a gas turbine. The product gas from an atmospheric pressure gasification process needs to be compressed before it is burned in a gas turbine and tars can condense in the compressor or in the transfer lines as the product gas cools. The purity of the gasification product gas for fuel cell applications varies considerably. Molten carbonate and solid oxide fuel cells with internal reforming capabilities may not require very stringent preconditioning of the fuel gas. Biomass gasification product gas will require substantial conditioning, including tar conversion or removal, before it is used in polymer electrolyte membrane (PEM) fuel cell systems that require essentially pure hydrogen. For catalytic synthesis of methanol and other liquid fuels, the gas composition should theoretically be adjusted to a $H_2:CO$ ratio of 2:1. The biomass gasification product gas will require conditioning to achieve this optimal gas composition.

Gas conditioning is a general term for removing the unwanted impurities from biomass gasification product gas and generally involves an integrated, multi-step approach that depends on the end use of the product gas. For the purpose of this report, the focus will be on removing or eliminating tars without regard to acid gas, ammonia, alkali metal, and particulate removal. In some cases, the strategies used for removing the various classes of impurities overlap.

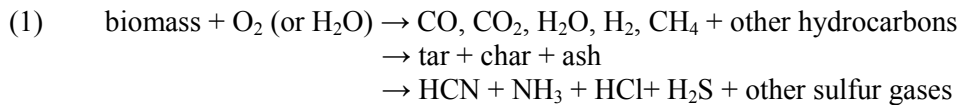
If the end use of the gas requires cooling to near ambient temperatures it is possible to use a number of physical removal methods, including wet scrubbing and filtration, to remove tars. Wet scrubbing is an effective gas conditioning process that condenses the tars out of the product gas. This technology is available and can be optimized for tar removal. A disadvantage of wet scrubbing for product gas conditioning is the formation and accumulation of wastewater. This technique does not eliminate tars but merely transfers the problem from the gas phase to the condensed phase. Wastewater minimization and treatment are important considerations when wet scrubbing is used for tar removal. Also, when tar is removed from the product gas stream, its fuel value is lost and the overall efficiency of the integrated gasification process is reduced. These issues associated with wet scrubbing can be reduced when it is used in conjunction with some level of catalytic hot gas conditioning.

If the end use requires that the product gas remain at high temperature, at or slightly below the gasifier exit temperature, then some method of hot gas cleaning will be needed for tar elimination. Wet scrubbing is still an option; however, a severe thermodynamic penalty will result from cooling and reheating the conditioned product gas, reducing the overall efficiency of the process. Hot gas conditioning eliminates tars by converting them into desired product gas components thus retaining their chemical energy in the product gas and avoiding treatment of an additional waste stream. Thermal cracking is a hot gas conditioning option but it requires temperatures higher than typical gasifier exit temperatures ($> 1100^{\circ}\text{C}$) to achieve high conversion efficiencies. Increased temperatures for thermal cracking tars can come from adding oxygen to the process and consuming some of the product gas to provide additional heat. Thermal destruction of tars may also produce soot that is an unwanted impurity in the product gas stream.

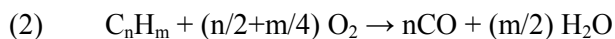
An attractive hot gas conditioning method for tar destruction is catalytic steam reforming. This technique offers several advantages: 1) catalyst reactor temperatures can be thermally integrated with the gasifier exit temperature, 2) the composition of the product gas can be catalytically adjusted, and 3) steam can be added to the catalyst reactor to ensure complete reforming of tars. Catalytic tar destruction has been studied for several decades [Mudge, et al. (1979, 1987, and 1988)] and a number of reviews have been written on biomass gasification hot gas cleanup [Stevens, (2001); Sutton, Kelleher, and Ross, (2001); and Milne, Abatzoglou, and Evans, (1998)]. Numerous catalysts have been tested for tar destruction activity at a broad range of scales. Novel catalyst formulations have been sought to increase the activity and lifetime of tar reforming catalysts. Different approaches for integrating catalytic tar destruction into biomass gasification systems have been investigated. The objective of this report is to summarize the literature pertaining to catalytic biomass gasification tar destruction, provide an overview of the different catalysts that have been studied and how they have been implemented, and evaluate the future potential of this gas cleaning technology.

BIOMASS GASIFICATION CHEMISTRY OVERVIEW

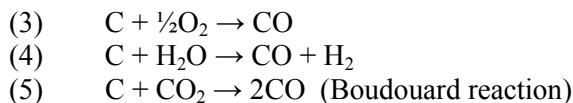
Biomass gasification is a complex thermochemical process that consists of a number of elementary chemical reactions, beginning with the partial oxidation of a lignocellulosic fuel with a gasifying agent, usually air, oxygen, or steam. Volatile matter, which is released as the biomass fuel is heated, partially oxidizes to yield the combustion products H_2O and CO_2 , plus heat to continue the endothermic gasification process. Water vaporizes and biomass pyrolysis continues as the fuel is heated. Thermal decomposition and partial oxidation of the pyrolysis vapors occur at higher temperatures, and yield a product gas composed of CO , CO_2 , H_2O , H_2 , CH_4 , other gaseous hydrocarbons (including oxygenated hydrocarbons from some processes), tars, char, inorganic constituents, and ash. A generalized reaction describing biomass gasification is as follows:



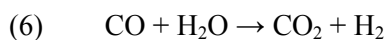
The actual biomass gasification product gas composition depends heavily on the gasification process, the gasifying agent, and the feedstock composition [Beenackers and van Swaaij, (1984); Hos and Groeneveld, (1987)]. Various gasification technologies have been under investigation for converting biomass into a gaseous fuel. These include gasifiers where the biomass is introduced at the top of the reactor and the gasifying medium is either directed co-currently (downdraft) or counter-currently up through the packed bed (updraft). Other gasifier designs incorporate circulating or bubbling fluidized beds. Tar yields can range from 0.1% (downdraft) to 20% (updraft) or greater (pyrolysis) in the product gases. The energy content of the gasification product gas ranges from 5 MJ/Nm^3 to 15 MJ/Nm^3 and is considered a low to medium energy content gas compared to natural gas (35 MJ/Nm^3). If air is used as the gasifying agent, then roughly half of the product gas is N_2 [de Bari, et al. (2000)]. The relative amount of CO , CO_2 , H_2O , H_2 , and hydrocarbons depends on the stoichiometry of the gasification process. The air/fuel ratio in a gasification process generally ranges from 0.2-0.35 and if steam is the gasifying agent, the steam/biomass ratio is around 1. The actual amount of CO , CO_2 , H_2O , H_2 , tars, and hydrocarbons depends on the partial oxidation of the volatile products, as shown in equation (2).



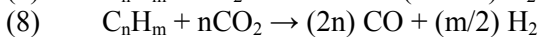
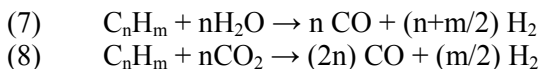
The char yield in a gasification process can be optimized to maximize carbon conversion or the char can be thermally oxidized to provide heat for the process. Char is partially oxidized or gasified according to the following reactions:



The gasification product gas composition, particularly the H_2 : CO ratio, can be further adjusted by reforming and shift chemistry. Additional hydrogen is formed when CO reacts with excess water vapor according to the water-gas shift reaction



Reforming the light hydrocarbons and tars formed during biomass gasification also produces hydrogen. Steam reforming and so-called dry or CO₂ reforming occur according to the following reactions and are usually promoted by the use of catalysts.



Catalytic steam reforming of hydrocarbons has been extensively studied, especially in the context of methane reforming to make syngas (H₂:CO = 2:1) for methanol and Fisher-Tropsch liquid synthesis. The basic mechanism of steam reforming is the dehydrogenation of a hydrocarbon fuel and the associated carbon deposition on the active sites of a catalyst. Gasification of the carbon deposits via reactions (3)-(5) yields additional CO and maintains the catalyst activity.

Similar catalysts have been applied to biomass gasifier tar reforming with varied success. Catalytic conversion of unwanted hydrocarbons is applied for both product gas purification and to adjust the composition of the product gases for a particular end use. Tar reforming also maintains the chemical energy content of the product gases because tars are converted to H₂ and CO and not physically removed.

CATALYTIC TAR DESTRUCTION STUDIES

Three groups of catalyst materials have been applied in biomass gasification systems – alkali metals, non-metallic oxides, and supported metallic oxides. Alkali metals are thought to enhance the biomass gasification reactions (eq. 1) and therefore are considered primary catalysts and not tar reforming catalysts. Alkali salts are mixed directly with the biomass as it is fed into the gasifier. It is well known from several fundamental studies of cellulose and biomass pyrolysis that alkali metals enhance char formation reactions during thermochemical conversion [Antal and Várhegyi, (1995); Raveendran et al., (1995 & 1996); Richards and Zheng, (1991)]. Poorer carbon conversion, increased ash content, and the fact that the added alkali metals are difficult to recover make alkali metals unattractive gasification catalysts for commercial use.

The non-metallic and supported metallic oxide catalysts are usually located in a separate fixed bed reactor, downstream from the gasifier, to reduce the tar content of the gasification product gas and are therefore, referred to as secondary catalysts. Although the non-metallic catalysts are sometimes used as bed material in fluidized bed gasifiers to affect tar formation, standalone catalytic reactors can be used with any gasification technology and can be independently controlled to maximize the versatility of the hot gas conditioning process. The most widely studied non-metallic catalysts for biomass gasifier tar conversion are dolomites - calcium magnesium carbonates. The success of reforming biomass gasification tars with supported Ni-based catalysts has also been extensively demonstrated. The literature associated with these two classes of catalysts is reviewed in the next sections.

Nonmetallic Oxides

Calcined dolomites have been extensively investigated as biomass gasifier tar destruction catalysts. These naturally occurring catalysts are relatively inexpensive and disposable so it is possible to use them as primary catalysts (in bed) as well as in secondary, downstream reactors.

Dolomite is a calcium magnesium ore with the general chemical formula CaMg(CO₃)₂ that contains ~20% MgO, ~30% CaO, and ~45% CO₂ on a weight basis, with other minor mineral impurities. Dolomites, in their naturally occurring form, are not nearly as active for tar conversion until they are calcined. Calcination of dolomite involves decomposition of the carbonate mineral, eliminating CO₂ to

form MgO-CaO. Complete dolomite calcination occurs at fairly high temperatures and is usually performed at 800°C-900°C. The calcination temperature of dolomite, therefore, restricts the effective use of this catalyst to these relatively high temperatures. Calcined dolomite also loses its tar conversion activity under conditions where the CO₂ partial pressure is greater than the equilibrium decomposition pressure of dolomite. This becomes an important issue in pressurized gasification processes. As the pressure of the process increases, the operating temperature of calcined dolomite reactor must be increased to maintain catalyst activity. Calcination also reduces the surface area of the dolomite catalyst and makes it more friable. Severe catalyst attrition and the production of fine particulate material plagues the use of calcined dolomite in fluidized bed reactors.

Several research groups have conducted extensive studies on the tar conversion effectiveness of calcined dolomites and other nonmetallic oxide catalysts. Simell and co-workers at VTT Energy in Finland, and Corella and co-workers at the University of Zaragoza and the University “Complutense” of Madrid have published numerous papers describing biomass gasifier tar conversion over calcined dolomite catalysts. A review of the earlier studies can be found in Delgado et al. (1996, 1997) and Sutton et al. (2001) and a summary of the literature, including catalyst composition, calcining and operating temperatures, feedstock and gasifier conditions, and reported conversion efficiencies can be found in Table 1.

Simell and co-workers performed a number of studies using model compounds as tar surrogates to test the reforming effectiveness of dolomites and other carbonate rocks. Simell, Leppalahti, and Kurkela (1995) evaluated the activities of Finnish and Swedish dolomites, dolomitic limestone, and SiC (reference material) for toluene decomposition at 900°C-1000°C and 2 MPa. The catalysts were calcined at 900°C and showed high toluene conversion efficiencies (>97%); however, catalyst activity was almost completely lost when the CO₂ partial pressure was higher than the equilibrium decomposition pressure of CaCO₃. Simell et al. (1997) also report a mechanistic model describing the catalytic decomposition of benzene over Finnish dolomite at similar conditions. Earlier studies by Simell and Bredenberg (1990) and Simell, Leppalahti, and Bredenberg (1992) describe the use of dolomites, limestones, and iron ores (ankerite and iron sinter) for reducing the tar content in the product gas stream from a peat-fired air-blown gasifier. Catalysts were operated at 900°C to condition a slipstream of the product gases. Tar destruction efficiencies ranged from 86% to > 99%. The activity of the dolomites and limestones increased as the Ca:Mg ratio increased, and the addition of iron increased activity further.

Corella and co-workers constructed a biomass gasification pilot plant to study catalytic product gas conditioning of both slipstreams and full gasifier output [Aznar et al. (1996), Narvaez et al. (1996)]. The fluidized bed gasifier (15-cm i.d.) had a throughput of approximately 10 kg/hr at gasification temperatures between 750°C-850°C. The gasifying agent was air, steam, and a mixture of steam and oxygen, and pine (*Pinus pinaster*) wood was fed into the bottom of the bubbling bed. The gasifier operation was optimized to minimize tar formation [Gil et al. (1999)] and a number of different strategies for hot gas cleanup were implemented. Olivares et al. (1997) described a 4-6-fold decrease in product gas tar content when 20g of calcined dolomite per kilogram of biomass was added to the gasifier bed. The hydrogen content of the product gas doubled and the CO content was reduced by a factor of two. Calcined dolomite, magnesite, and calcite in a downstream reactor operating between 800°C-880°C were also studied in this pilot plant [Delgado et al. (1996) and (1997)]. Catalyst deactivation was observed (during 14 h tests) and kept to a minimum at high temperatures (> 840°C). Tar conversions were initially 99% and decreased as the catalysts deactivated. Additional, more comprehensive results for Malaga dolomite in a downstream catalyst reactor are reported in Perez et al. (1997).

Several other groups have also studied catalytic tar reforming with nonmetallic oxides. Taralas and co-workers in Sweden [Taralas (1997) and Taralas et al. (1991)] used calcined dolomite, quicklime, and dolomitic magnesium oxide to reform cyclohexane and n-heptane as model tar compounds. Vassilatos et al. (1992) used calcined dolomite at 700°C-900°C to catalytically condition biomass pyrolysis vapors.

All of these studies demonstrate that dolomite is a very effective tar reforming catalyst. High molecular weight hydrocarbons are efficiently reformed at moderately high temperatures ($> 800^{\circ}\text{C}$) with steam and oxygen mixtures as the gasifying agent; however, the output methane concentration is not greatly affected and benzene and naphthalene are often not completely reformed. This highlights the effective use of dolomite in a guard bed prior to catalyst reactors containing other metallic reforming catalysts. High steam concentrations in the product gas, short space times, and high temperatures help to improve the lifetime of the calcined dolomite because the kinetics of steam gasification of carbon are fast enough to remove coke as it is formed on the catalyst surface. Many investigators have also reported a decrease in the mechanical strength of the calcined dolomite over time, which leads to catalyst attrition.

An interesting alternative to calcined dolomite is olivine, a magnesium aluminosilicate. Rapagna et al. (2000) have found the tar reforming activity of olivine comparable to calcined dolomite. Olivine, however, is a much stronger material and resists attrition in fluidized bed reactors. Olivine is an attractive material for use as an in-bed tar reforming catalyst in fluidized bed gasifiers.

Commercial Nickel Reforming Catalysts

A wide variety of Ni-based steam reforming catalysts are commercially available because of their application in the petrochemical industry for naphtha reforming and methane reforming to make syngas. Nickel-based catalysts have also proven to be very effective for hot conditioning of biomass gasification product gases. They have high activity for tar destruction, methane in the gasification product gas is reformed, and they have some water-gas shift activity to adjust the $\text{H}_2:\text{CO}$ ratio of the product gas. The H_2 and CO content of the product gas increases, while hydrocarbons and methane are eliminated or substantially reduced for catalyst operating temperatures above $\sim 740^{\circ}\text{C}$. Some studies have also shown that nickel catalyzes the reverse ammonia reaction, thus reducing the amount of NH_3 in gasification product gas.

The simplified mechanism for catalytic tar reforming can be described as follows [Garcia et al. (2000)]. First, methane or other hydrocarbons are dissociatively adsorbed onto a metal site where metal-catalyzed dehydrogenation occurs. Water is also dissociatively adsorbed onto the ceramic support, hydroxylating the surface. At the appropriate temperature, the OH radicals migrate to the metal sites, leading to oxidation of the intermediate hydrocarbon fragments and surface carbon to $\text{CO} + \text{H}_2$.

The routine use of nickel catalysts for hot gas conditioning of biomass gasification product gases is limited by deactivation caused by several factors. Sulfur, chlorine, and alkali metals that may be present in gasification product gases act as catalyst poisons. Coke formation on the catalyst surface can be substantial when tar levels in product gases are high. Coke can be removed by regenerating the catalyst, however, repeated high temperature processing of nickel catalysts can lead to sintering, phase transformations, and volatilization of the nickel.

The literature contains numerous studies detailing the use of commercial Ni-based catalysts for tar reforming. These studies are summarized in Table 2, with catalyst names, compositions (when available), operating temperatures, biomass feedstock, gasifier operating conditions, and tar conversion efficiencies. Catalyst formulations differ by the loading of Ni used, the composition of the support material, and the trace amounts of various promoters that are incorporated into the matrix.

Nickel catalysts have been tested as primary (in-bed) catalysts in an attempt to reduce the tar levels in gasification product gas with little success [Baker et al. (1987)]. Coke formation and catalyst attrition led to rapid loss of tar conversion activity. Consequently, these metallic catalysts are typically used in

secondary fixed bed catalyst reactors. In many cases, they are used in conjunction with calcined dolomite catalysts in guard beds for the highly active nickel catalysts. Nickel, and other transition metals, are also used in novel formulations that have been optimized for tar reforming. These research formulations are discussed in the next section.

Not too surprising, the two groups that were active in studying calcined dolomite catalysts have also published results from many studies involving nickel steam reforming catalysts for hot gas conditioning. Between 1997-1999, Corella and co-workers published a number of papers detailing the use of commercial steam reforming catalysts for tar conversion in their biomass gasification pilot plant [Corella et al. (1997), (1998), (1999); Navarez et al. (1997); Caballero et al. (2000)]. For most of the studies, a calcined dolomite guard bed was used to reduce the initial level of tars from the gasifier. Catalyst temperatures were maintained between 750°C-850°C and initial tar conversion efficiencies were greater than 99%. An apparent kinetic rate for tar reforming was determined for each catalyst tested based on a first order rate expression and the measured tar conversion as a function of time-on-stream. Deactivation began after only a few hours time-on-stream in many cases, but some catalysts performed for more than 100 hours without showing signs of deactivation.

Simell and co-workers have also investigated commercial Ni steam reforming catalysts for tar conversion. They used toluene as a model tar compound in several studies to investigate the effectiveness of Ni/Al₂O₃ catalysts at elevated pressures. Simell, Hepola, and Krause (1997) report the use of 18% Ni on alumina, and other catalysts with variable Ni content, operating at 900°C and 0.5-20 MPa to reform toluene in various gas atmospheres. Ammonia decomposition via the reverse ammonia reaction (to form H₂ and N₂) was postulated, in addition to evaluating the tar conversion effectiveness of the various catalysts. The effects of sulfur poisoning on the activity of these catalysts for tar and ammonia decomposition have also been reported [Hepola and Simell, (1997a,b)]. The ammonia conversion activity was more sensitive to sulfur poisoning than the tar conversion activity. The high catalyst operating temperature helps to avoid deactivation by coke formation and minimizes the effect of sulfur poisoning. The catalyst activity for tar conversion was quickly recovered when sulfur was removed from the gas mixture, but the ammonia conversion efficiency was not completely regained.

This group has also investigated the use of a novel, commercially available (BASF AG) Ni monolith catalyst [Simell et al. (1997); Simell and Kurkela (1997); Simell et al. (1996)]. The square monolith support is 30-cm x 5-cm x 5-cm with square channels; the specific details of this catalyst are proprietary. This catalyst has been tested in a pressurized gasification process using various gasifier feedstocks such as wood waste, bark wood chips, and peat. Varying tar, ammonia, and sulfur concentrations in the products gases resulted. The authors claim that this catalyst reactor does not plug when conditioning product gases with high particulate loadings and can be used without prior particulate removal. Complete tar decomposition and an average of 80% ammonia conversion were reported for catalyst operating temperatures of 900°C and 5 MPa. The Ni monolith catalyst activity did not measurably decrease during a 500 h test. Further study of this catalyst is warranted as more details of the catalyst formulation and structure become available.

Kinoshita, Wang, and Zhou (1995) report the results from parametric studies on catalytic reforming of tars produced in a bench-scale gasification system. A commercial Ni catalyst (UC G-90B) was tested at various temperatures (650°C-800°C), space times (0.6-2.0 s), and steam/biomass ratios (0-1.2) in a fluidized bed catalytic reactor. They report optimum conditions for achieving 97% tar conversion and increased product gas yields. Gebhard et al. (1994) report the reforming of a synthetic tar mixture (representative of the measured tar composition for an indirect gasifier) using a commercial Ni reforming catalyst.

Bangala et al. (1997) also report on the effectiveness of a commercial Ni steam reforming catalyst compared to their proprietary novel Ni catalyst formulation for naphthalene conversion. Depner and Jess (1999) report the use of Süd Chemie G 117, a commercial Ni catalyst, for the conversion of benzene and naphthalene in various gas mixtures, including H₂S, between 450°C-1150°C at slightly elevated pressure (160 kPa). They report kinetic parameters for simulating commercial-scale catalyst reactors based on their bench-scale results. Coll et al. (2001) report on the steam reforming of the model compounds benzene, toluene, naphthalene, anthracene, and pyrene using two commercial nickel catalysts: UC G90-C and ICI 46-1. Catalyst temperatures varied between 700°C-800°C and optimum steam/carbon ratios were determined for each model compound. Naphthalene had the slowest steam-reforming rate and the most reactive compound of the group was benzene. Coke formation increased as the molecular weight of the model compound increased.

Commercial Ni reforming catalysts have been applied in a number of model compound and novel feedstock studies for the purpose of producing a hydrogen-rich product gas, not necessarily for tar reforming, although typical tar compounds are often included in the feed. Wang, Montane, and Chornet (1996) used a commercial steam reforming catalyst and a low temperature shift catalyst to produce high yields of hydrogen from acetic acid and hydroxyacetaldehyde. Both compounds were completely steam reformed between 300°C-700°C. Coke formed on the catalyst during acetic acid reforming but not during hydroxyacetaldehyde reforming. Wang et al. (1998) also studied H₂ production from biomass pyrolysis oil steam reforming using a variety of commercial nickel catalysts. Garcia et al. (2000) also report the use of commercial and research nickel-based catalysts for steam reforming the aqueous fraction of biomass pyrolysis oil to yield a H₂-rich product gas.

Optimized Research Catalyst Formulations

Evaluating the effectiveness of commercial steam reforming catalysts for tar conversion provides an excellent starting point for developing novel catalyst formulations to optimize desired catalyst properties. A summary of the literature from studies that describe novel catalyst formulations for reforming biomass tars and model compounds is presented in Table 3. Catalyst formulation, operating conditions, feedstocks used, and reported conversion efficiencies are listed.

The commercial success of Ni reforming catalysts has prompted several studies focused on developing additional nickel-based catalysts for biomass gasification applications. Arauzo et al. (1994) developed a nickel aluminate (33% Ni) catalyst for improving the gas yields in the Waterloo Fast Pyrolysis Process for biomass pyrolysis. Garcia et al. (1999) used a 1:2 Ni:Al co-precipitated catalyst in the same process to optimize gas yields of the gasification of pine sawdust at 700°C.

Courson et al. (2000) attempted to combine the demonstrated activity of olivine for biomass tar reforming and the success of Ni steam reforming catalysts by developing an olivine supported nickel catalyst. Nickel was impregnated in natural olivine to prepare catalysts that contained 2.8 wt% Ni after calcining in air at 900°C, 1100°C, and 1400°C. Methane dry and steam reforming with the Ni/olivine catalysts were evaluated at 600°C-850°C. The catalyst calcined at 1100°C had the highest activity (95%) for methane conversion.

Sutton et al. (2001) studied the effect of catalyst support on the activity of Ni-based catalysts for peat gasification tar conversion. Peat was gasified in a fixed bed, plug flow quartz reactor in N₂, at an ultimate temperature of 550°C. A second fixed bed plug flow reactor downstream of the first was charged with the prepared Ni catalysts and maintained at 800°C. Catalysts were prepared by impregnating Ni in a variety of different supports, including: Al₂O₃, ZrO₂, TiO₂, SiO₂, and MOR1, a proprietary tar-destruction catalyst. The calcined catalysts contained 5wt% Ni. Two additional catalysts were prepared by co-

precipitating Ni and Al with molar ratios of 3:17 and 1:3 Ni:Al. High gas conversions were measured for all of the prepared catalysts; however, the co-precipitated catalysts were the most active. This group [Sutton, Parle, and Ross (2002)] also compared the activity of the 3:17 Ni/Al co-precipitated catalyst with 1 wt% Ru/Al₂O₃ and 1 wt% Pt/ZrO₂ for dry (CO₂) reforming CH₄ and C₃H₈ at 450°C-800°C.

Draelents et al. (2001 and 2000a,b) have also utilized additional supports for Ni catalysts. This group has investigated different methods for introducing Ni into ceramic candle filters to combine tar reforming and efficient particle removal. Up to 2 wt% Ni has been added to alumina candle filter disks and evaluated for converting benzene and naphthalene as model tar compounds in synthetic gasification product gas. Operating temperatures of 750°C-900°C with typical gas velocities found in candle filters resulted in 67% benzene conversion and almost complete conversion of naphthalene.

As discussed in the previous section, several limitations of Ni reforming catalysts for gasifier tar conversion are deactivation by coke formation, sulfur and chlorine poisoning, and sintering. Adding various promoters and support modifiers has been attempted by several groups to improve catalyst activity, lifetime, poison resistance, and resistance to coke formation. Bangala, et al. (1997 and 1998) described the development of a catalyst formulation named UdeS that incorporates a rare earth oxide in an alumina matrix and a metal promoter for prolonged activity in biomass gasification product gases with high tar loadings. The resulting formulation is described in Bangala and Chornet (1994) and consists of a Ni-Cr catalyst supported on γ -alumina doped with MgO and La₂O₃. The addition of Cr to the catalyst helps to maintain the Ni in the proper phase by inhibiting NiC formation. Adding MgO to the alumina support leads to the formation of MgAl₂O₄ spinel that is more robust than alumina. Introduction of La₂O₃ in the support decreases the rate of carbon deposition by promoting the steam gasification of carbon on the catalyst surface. An excellent description of the effects of various promoters and modifiers can be found in Bangala, Abatzoglou, and Chornet (1998) and the references cited therein. Initial performance of this catalyst was found to be excellent with high measured conversion efficiency and minimal deactivation after 100 h.

Rapagna et al. (2002) developed a similar catalyst with a chemical formula of LaNi_{0.3}Fe_{0.7}O₃ that was prepared by means of a sol-gel related process where La, Ni, and Fe nitrate salts were dissolved separately in hot propionic acid. The nickel and iron solutions are mixed together first and then added to the lanthanum solution. The prepared catalyst displayed high CH₄ reforming activity at 800°C resulting in 90% CH₄ conversion. This catalyst was also tested in a secondary catalytic reactor operating at 800°C downstream of a fluidized bed gasifier. Almond shells were gasified at 770°C in a bed of olivine with a steam:biomass ratio of 1. A 90% tar conversion was measured.

Garcia et al. (2000) have prepared a number of different Ni-based catalysts for optimal hydrogen production from the catalytic steam reforming of biomass pyrolysis oils. The goal was to develop a modified catalyst to combat deactivation by carbon deposition. Two different approaches were taken. One approach was to modify the support to enhance steam adsorption and thereby increase surface carbon gasification rates. The second approach was to add metal promoters to reduce the rate of carbon deposition. The base catalyst in these studies was Ni on an α -Al₂O₃ support. Magnesium and lanthanum were added as support modifiers to achieve the first goal of enhanced steam adsorption. Cobalt and chromium were added to reduce coke formation. The cobalt-promoted and chromium-promoted nickel catalysts on a MgO-La₂O₃- α -Al₂O₃ support performed the best in terms of H₂ yield and lifetime.

Asadullah and co-workers [Asadullah et al. (2002) and (2001a,b)] have developed Rh-based catalysts to enhance the low temperature gasification of cellulose and biomass. In the first paper in the series [Asadullah et al. (2001a)], catalysts with Rh, Ru, Pt, Pd, and Ni on ceria were used in a bench-scale fluidized bed reactor to gasify cellulose in air at 550°C. The metal loading for all of the catalysts was 1.2x10⁻⁴ mol/g-cat. Carbon conversions to gas ranged from 80%-100%, with the Rh/CeO₂ catalyst

performing the best. The following study tested Rh catalysts on various support materials [Asadullah et al. (2001b)], including CeO₂, ZrO₂, Al₂O₃, MgO, and SiO₂, for low temperature cellulose gasification. Carbon conversions to gas ranged from 68%-100% with the Rh/CeO₂ catalyst again exhibiting the best performance. The Rh catalyst was further modified by the addition of SiO₂ in the support, yielding a Rh/CeO₂/SiO₂ catalyst with 35 wt% SiO₂ [Asadullah et al. (2002)].

SUMMARY and RECOMMENDATIONS

This report provides a review of the literature pertaining to catalytic reforming of tars formed during biomass gasification. Two forms of catalysts, nonmetallic and metallic, have proven effectiveness for tar conversion. Dolomites are the most widely used nonmetallic catalysts for tar conversion in biomass gasification processes, but only show tar conversion activity after they are calcined. They are relatively inexpensive and are considered disposable. Tar conversion efficiency is high when dolomites are operated at high temperatures (900°C) with steam. Calcined dolomites are not very robust and quickly undergo attrition in fluidized bed reactors. As a result, calcined dolomite is not an effective primary, or in-bed, catalyst, but has found use in secondary catalyst beds, particularly in guard beds prior to more active Ni reforming catalyst reactors. Olivine, another naturally occurring mineral has also demonstrated tar conversion activity similar to that of calcined dolomite. Olivine is a much more robust material than calcined dolomite and has been applied as a primary catalyst to reduce the output tar levels from fluidized bed biomass gasifiers. Olivine appears to be an appropriate bed material for fluidized bed gasifiers regardless of other hot gas conditioning methods.

Commercial Ni steam reforming catalysts have also been widely used for biomass gasification tar conversion. They have high, demonstrated activity for tar destruction with the added advantages of completely reforming methane and water-gas shift activity that allows the H₂:CO ratio of the product gas to be adjusted. Some studies have also shown that nickel catalyzes the reverse ammonia reaction thus reducing the amount of NH₃ in gasification product gas.

Commercial Ni catalysts are not mechanically robust and are designed primarily for use in fixed bed reactors. Consequently, Ni catalysts have been most effectively used as secondary catalysts in separate fixed bed reactors downstream from the gasifier. This provides additional process flexibility because the catalyst can be operated independently and its performance optimized. In many processes, a calcined dolomite guard bed will be used to lower the tar levels in the product gas prior to the Ni reforming catalyst.

A limitation of nickel catalyst use for hot gas conditioning of biomass gasification product gases is rapid deactivation, which leads to limited catalyst lifetimes. Ni catalyst deactivation is caused by several factors. Sulfur, chlorine, and alkali metals that may be present in gasification product gases act as catalyst poisons. Coke formation on the catalyst surface can be substantial when tar levels in product gases are high. Coke can be removed by regenerating the catalyst, however, repeated high temperature processing of nickel catalysts can lead to sintering, phase transformations, and volatilization of the nickel. Repeated disposal of spent Ni catalysts is not economical and poses an environmental hazard because of the toxicity of nickel.

As mentioned, using dolomite guard beds to lower the input tar concentration can extend Ni catalyst lifetimes. Adding various promoters and support modifiers has been demonstrated to improve catalyst lifetimes by reducing catalyst deactivation from coke formation, sulfur and chlorine poisoning, and sintering. Several novel, Ni-based catalyst formulations have been developed that show excellent tar reforming activity, improved mechanical properties for use in fluidized bed reactors, and enhanced

lifetimes. Several of these proprietary research catalysts warrant additional investigation for specific individual gasification processes.

A critical gap identified for catalytic tar reforming technology in biomass gasification processes is the need for extended lifetime studies of promising commercial or novel catalysts. Catalytic hot gas conditioning will not become a commercial technology unless adequate catalyst lifetimes can be demonstrated, even for inexpensive, disposable catalysts like calcined dolomite. Frequent disposal of dolomite generates an additional waste stream and disposal of toxic spent Ni catalysts becomes an environmental burden. Assessment of catalyst lifetimes will allow biomass gasification developers to accurately evaluate the cost of this unit operation. The effects of catalyst poisons like sulfur, chlorine, and alkali metals and continued catalyst regeneration can be critically evaluated with long-term catalyst testing. Understanding these effects will enable the proper selection of gas conditioning technology matched to the desired end-use application of the biomass gasification product gas. Accurate catalyst cost and lifetime figures will provide important input for techno-economic analyses of developing gasification technologies.

Hot gas conditioning using current and future commercially available catalysts offers the best solution for mitigating biomass gasification tars. Tars are eliminated, methane can be reformed if desired, and the H₂:CO ratio can be adjusted in a single step. Production of a new wastewater stream is avoided and, by reforming the tars at temperature, the thermodynamic efficiency of the integrated process is maintained because the gasifier and gas conditioning step are thermally integrated and the chemical energy of the converted tars remains in the product gas. The best currently available tar reforming process consists of a calcined dolomite guard bed followed by a fixed bed Ni catalyst reforming reactor operating at about 800°C. This dual bed hot gas conditioning concept has been demonstrated and can be used to condition the product gas from any developing gasification process; however, selection of the ideal Ni catalyst is somewhat premature. Commercially available steam reforming catalysts have been demonstrated, but several novel research catalysts appear to have the potential of longer lifetimes that should be verified. Several of these research catalysts also have improved mechanical strength making fluidized bed applications feasible. For fluidized bed gasifiers, the guard bed could potentially be eliminated if olivine is used as the bed material. The proprietary Ni monolith catalyst also warrants future consideration.

Table 1: A summary of properties and effectiveness of Nonmetallic catalysts used for tar destruction

| Material (Name) | Composition (wt%) | | | | | | | Space Time/ velocity | Operating Temp (°C) | Feedstock composition | X _{tar} (%) | References |
|-------------------------|-------------------|-----------|------------------|--------------------------------|--------------------------------|-----------------|---|--|-------------------------|--|----------------------|--|
| | MgO | CaO | SiO ₂ | Fe ₂ O ₃ | Al ₂ O ₃ | CO ₂ | Other | | | | | |
| Dolomite Norte | 20.9 | 30.9 | 1.7 | 0.5 | 0.6 | 45.4 | | 0.079-0.32 kgh/Nm ³ (1800-7200 1/h) | 800-880 840-912 | Pine; S/B= 1.1 @ 750-780C | 60-99 | Delgado, et al. 1996 Delgado, et al. 1997 |
| Calcite Morata | 0.6 | 53.0 | 2.7 | 0.8 | 1.0 | 41.9 | | | | | 70-99 | |
| Magnesite Navarra | 47.1 | 0.7 | --- | --- | --- | 52.0 | | | | | 10-99 | |
| Finnish dolomite | 18.3 | 26.6 | 5.4 | 2.1 | 1.1 | 42 | 0.5 TiO ₂ ; 0.5 NiO | 550-1150 kgcath/h/kmol | 750-900 | C ₆ H ₆ (50-500ppm) in N ₂ + CO ₂ (0.06-10 vol%) | | Simell, et al. 1997 |
| Limestone | 0.33 | 55.3 | 0.38 | 0.076 | 0.074 | | 0.074 Na ₂ O; 0.013 K ₂ O | 1-7 s | 720-790 | Pet. distillation resid; coke oven tar; coal tar | 20-99 | Garcia, et al. 1999 |
| Dolomite Norte | 18.7 | 32.2 | 3.3 | 0.12 | 0.06 | 45.5 | 0.01 K ₂ O & Na ₂ O; 0.09 MnO | 0.23-0.39 s | 780-920 | Pine gasification, ER=0.2-0.5 | 78-91 | Orio et al. 1997 |
| Dolomite Chilches | 17.5-19.0 | 29.7-31.3 | 3.2 | 0.74-0.80 | 1.19 | 47.4 | 0.24 K ₂ O; 0.05 Na ₂ O; 0.04 MnO | | 780-920 | | 87-97 | |
| Dolomite Malaga | 21.2 | 30.6 | --- | 0.01 | 0.40 | 47.3 | | | 780-920 | | 71-92 | |
| Dolomite Sevilla | 21.5 | 30.5 | --- | 0.01 | 0.60 | 47.2 | | | 780-920 | | 91 | |
| Dolomite Malaga | 21.2 | 30.6 | --- | 0.01 | 0.40 | 47.3 | | 0.05-0.25 kgh/m ³ | 840 | Pine gasification: (H ₂ O+O ₂)/biomass = 0.7-1.6; H ₂ O/O ₂ = 2-3 | 75-96 | Perez et a. 1997 |
| DN-34 | | | | | γ 100 | | | 1500-2500 1/h | 650 & 815 | Synthetic tar in He/H ₂ O | 20-90 | Gebhard, et al. 1994 |
| Dolomite Malaga | 21.2 | 30.6 | --- | 0.01 | 0.40 | 47.3 | | 0.95-1.55 s | 795-835 In gasifier bed | Pine +3% dolomite: (H ₂ O+O ₂)/biomass = 0.7-1.2; H ₂ O/O ₂ = 2-3 | 75 | Olivares et al. 1997 |
| Olivine Magnolithe GmbH | 48-50 | | 39-42 | 8-10 | | | | 0.1-1.25 kgh/m ³ | 700-820 In gasifier bed | Almond shells S/B=0.5-1 T=700-820 | ~90 | Rapagna et al. 2000 |

| Material (Name) | Composition (wt%) | | | | | | | Space Time/velocity | Operating Temp (°C) | Feedstock composition | X _{tar} (%) | References |
|------------------------------|-------------------|------|------------------|--------------------------------|--------------------------------|-----------------|--------------------------------|---------------------|---------------------|---|---|--|
| | MgO | CaO | SiO ₂ | Fe ₂ O ₃ | Al ₂ O ₃ | CO ₂ | Other | | | | | |
| Alumina | | | | | α 100 | | | 0.007-0.3 s | 900 | Toluene in N ₂ , H ₂ , CO, CO ₂ , CO ₂ +H ₂ O, and CO+CO ₂ @ 0.5 -20 MPa | | Simell, Hepola, Krause 1997 |
| Dolomite Kalkkima | 18.3 | 26.6 | 5.4 | 2.1 | 1.1 | 42 | 0.5 TiO ₂ ; 0.5 NiO | | | | | |
| Dolomite Myanti | 17.8 | 26 | 2.8 | 0.4 | 0.4 | 44 | 0.1 K+Na | 0.4 s | 900-1000 | Toluene in 10 vol% H ₂ O +CO ₂ /N ₂ @ 2 Mpa and 48% N ₂ , 10% H ₂ , 11% CO, 14% CO ₂ , 5% CH ₄ , 12% H ₂ O + 15 g/Nm ³ toluene | 86-97 for C ₇ H ₇ , 30-60 for other | Simell, Leppalahti, and Kurkela 1995 |
| Dolomite Kalkkima | 16 | 21 | 7 | 1.1 | 1.5 | 42 | 0.7 K+Na | | | | | |
| Dolomitic limestone Parainen | 1 | 46 | 2 | 0.14 | 0.6 | 48 | 0.2 K+Na | | | | | |
| Silica-alumina | | | 86.5 | | 13 | | | 0.2-0.3 s | 900 | Sod peat updraft gasification air/fuel = 1.55 | | Simell and Bredenberg, 1990 |
| Activated alumina | | | | | 99 | | | | | | | |
| Dolomite Vimpeli | 12 | 29 | 10.5 | | | | | | | | | |
| Limestone Gotland | 0.1 | 48 | 1.1 | 0.1 | 0.4 | 49 | | 0.1-1.5 s | 900 | Sod peat updraft gasification air/fuel = 1.55 | 99.5 | Simell, Leppalahti, and Bredenberg, 1992 |
| Limestone Parainen | 1 | 46 | 2 | 0.1 | 0.5 | 49 | | | | | 97 | |
| Dolomite Loukolampi | 16 | 24 | 14 | 0.3 | 7 | 39 | | | | | 98.6 | |
| Dolomite Kalkkima | 18 | 24 | 8 | 1.3 | 1.7 | 48 | | | | | 99 | |
| Ankerite | 14 | 28 | 0.6 | 7 | | 49 | | | | | 99 | |
| Iron Sinter | 2.3 | 7.6 | 4.7 | 85 | 0.4 | | | | | | 91 | |
| Pelletized iron ore | 0.5 | 1.4 | 1.2 | 96 | 1 | | | | | | 86 | |
| Dolomite Sala | 18.8 | 31.1 | 4.7 | | | 44 | | 0.17-0.75 s | 700-800 | n-heptane:steam = 3:1 in N ₂ | 23-88 | Taralas et al. 1991 |
| Dolomite Glanshammar | 19.7 | 29.5 | 5.9 | | | 44 | | | | | 24-80 | |
| CaO | | 100 | | | | | | | | | 20-96 | |
| MgO | 100 | | | | | | | | | | 30-97 | |

Table 2: A summary of the effectiveness of commercial Nickel steam reforming catalysts used for biomass tar destruction

| Catalyst Name | Composition (wt%) | | | | | | | Space Time/velocity | Operating Temp (°C) | Feedstock composition | X _{tar} (%) | References |
|---------------------|-------------------|-----|-----|------------------|--------------------------------|------------------|--------------------------------------|--------------------------------|---------------------|--|----------------------|----------------------------------|
| | NiO | MgO | CaO | SiO ₂ | Al ₂ O ₃ | K ₂ O | Other | | | | | |
| BASF G1-25/1 | 25 | --- | 8 | <0.2 | 66 | 1 | | 0.014-0.127 kgh/m ³ | 805* | Pine gasification in air ER = 0.23 T=805C | ≤99 | Corella, et al. 1997, 1998, 1999 |
| BASF G1-50 | 20 | 11 | 16 | 14 | 32 | 7 | | | 800-820* | Pine gasification in air ER = 0.26 T=800C | ≤99 | |
| ICI 46-1P | 22 | 11 | 13 | 16 | 26 | 7 | | | 800-810* | Pine gasification in air ER = 0.28 T=800C | ≤99 | |
| ICI 57-3 | 12 | | 10 | 0.1 | 78 | | | | 740* | Pine gasification in air ER = 0.33 T=800C | ≤99 | |
| Haldor Topsoe RKS-1 | 15 | | | 0.1 | | <0.05 | 85% MgAl ₂ O ₄ | | 800* | Pine gasification in air ER = 0.34 T=775C | ≤99 | |
| Haldor Topsoe R-67 | 15 | | | 0.1 | | <0.05 | 85% MgAl ₂ O ₄ | | 800* | Pine gasification in air ER = 0.28 T=710C | ≤99 | |
| UCI C11-9-061 | 10-15 | | | | 80-90 | | | | 750-800* | Pine gasification in air ER = 0.39 T=810 | ≤99 | |
| BASF G1-25S | 15 | | | | 85 | | | 0.09-1.2 s | 650-720* | Pine gasification in air ER = 0.2-0.45 | 88-97 | Navarez et al. 1997 |
| ICI 46-1 | 22 | 11 | 13 | 16 | 26 | 7 | | 1500-2500 l/h | 600&900 | Synthetic tar in He/H ₂ O | | Gebhard et al. 1994 |
| NCM (W.R. Grace) | 12 | | | Support | | | 4.25% CuO 9.25% MoO ₃ | 2-3 s | 750 | Steam gasification of wood T=750 | | Baker et al. 1987 |
| UC G-90C | 15 | | 6-9 | | 70-76 | | | | 750 | | | |
| ICI 46-1 | 21 | 13 | 13 | 14 | 29 | 7 | | | 750 | | 90 | |
| UC G-90B | 11 | | 6-9 | | 76-82 | | Ceramic support | 0.6-2.0 s | 650-800 | Sawdust T=800C ER=0.27 S/B=0-1.2 | 97 | Kinoshita, Wang, and Zhou, 1995 |

| Catalyst Name | Composition (wt%) | | | | | | | Space Time/velocity | Operating Temp (°C) | Feedstock composition | X _{tar} (%) | References |
|-----------------------------------|-------------------|-----|------|------------------|--------------------------------|------------------|---|------------------------------------|---------------------|---|----------------------|--|
| | NiO | MgO | CaO | SiO ₂ | Al ₂ O ₃ | K ₂ O | Other | | | | | |
| UC G-90C | 15 | | 6-9 | | 70-76 | | | 0.0004-0.0237 kgh/m ³ | 750-875 | Benzene, toluene, naphthalene, anthracene, pyrene | | Coll, et al. 2001 |
| ICI 46-1 | 22 | 11 | 13 | 16 | 26 | 7 | | | 700-800 | | | |
| Ni/Al ₂ O ₃ | 18 | | | 0.25 | 81 | | | 0.007-0.3 s | 900 | Toluene in N ₂ , H ₂ , CO, CO ₂ , CO ₂ +H ₂ O, and CO+CO ₂ @ 0.5 -20 MPa | | Simell, Hepola, Krause 1997 |
| BASF G1-50 | 20 | 11 | 16 | 14 | 32 | 7 | | 0.15-0.32 s | 830* | | 98 | Caballero et al. 2000 |
| Haldor Topsoe R-67 | 15 | | | 0.1 | | <0.05 | 85% MgAl ₂ O ₄ | | 835-840* | | 95-96 | |
| ICI 46-1 | 22 | 11 | 13 | 16 | 26 | 7 | | | 830-850* | | 99 | |
| Nickel A1 | 18 | | | | 81 | | 0.06 Fe ₂ O ₃ | 3500-30000 1/h (nominal 15000 1/h) | 800-950 | 0.48 N ₂ , 0.1 H ₂ , 0.11 CO, 0.14 CO ₂ , 0.05 CH ₄ , 0.05 H ₂ O, 0.12 4400 ppmv NH ₃ , 3200 ppmv toluene, 0-440 ppmv H ₂ S @ 1-20 bar | 20-99 | Hepola and Simell 1997a,b |
| Nickel A2 | 15 | | | | 84 | | 0.07 Fe ₂ O ₃ , 0.1 Na ₂ O | | | | | |
| Nickel B | 2 | | | | 97 | | 0.5 SO ₃ , 0.2 Na ₂ O | | | | | |
| Nickel C | 30 | | 10.5 | 0.4 | 54 | | 0.1 Fe ₂ O ₃ , 0.15 Na ₂ O | | | | | |
| Engelhard NI-3288 | 50 | | | | 50 | | | na | 260-350 | Cellulose in water @ 3 MPa | | Minowa and Ogi 1998 |
| BASF Ni Monolith | ? | | | | | | 300 mm x 50 mm x 50mm | 2200-2800 1/h | 880-960 | 1-7 g/Nm ³ tar 600-6000 ppmv NH ₃ 30-250 ppmv H ₂ S in a mixture of N ₂ , H ₂ , CO, CO ₂ , CH ₄ and H ₂ O @ 5 bar | 99 | Simell et al. 1997conf, Simell and Kurkela 1997, Simell et al 1996 |
| Süd-Chemie G 117 | 6 | 94 | | | | | | 0.1 s | 450-1150 | Naphthalene, benzene, CH ₄ in fed gas at 160 kPa | 0-99 | Depner and Jess 1999 |

| Catalyst Name | Composition (wt%) | | | | | | | Space Time/velocity | Operating Temp (°C) | Feedstock composition | X _{tar} (%) | References |
|---------------|-------------------|-----|-----|------------------|--------------------------------|------------------|-----------------------------------|-----------------------------|---------------------|-------------------------------------|----------------------|--------------------------------|
| | NiO | MgO | CaO | SiO ₂ | Al ₂ O ₃ | K ₂ O | Other | | | | | |
| UC G-90C | 15 | | 5-8 | | 70-76 | | | ~2000 1/h or 0.05-0.2 s | 300-700 | HAc and HAA in He | | Wang, Montane, Chornet 1996 |
| UC C18HC | | | | | 11 | | 42% CuO 47% ZnO | | 300-700 | | | |
| UC G-91 | 11 | | 6-9 | | 76-82 | | | 126000 1/h | 825-875 | Poplar bio-oil: aqueous fraction | | Garcia et al. 2000 |
| ICI C11-NK | 11- 20 | | | | | | | | 825-875 | Poplar bio-oil: aqueous fraction | | |
| UC G-98B | 55 | | | | 31 | | 5% CuO, 6% MoO ₃ | 0.31-0.82 s or 10080 1/h | 600-850 | steam/naphthalene | 40- 100 | Bangala et al. 1997 |

*Dolomite guard bed used

Table 3: A summary of novel catalysts formulations for biomass gasifier tar destruction

| Catalyst (Name) | Composition (wt%) | | | | | | | | Operating Temp (°C) | Space time/ velocity | Feedstock composition | X _{tar} (%) | References |
|---|-------------------|-----|-----|------------------|--------------------------------|--------------------------------|----------------------|------------------------------------|---------------------|----------------------|---|----------------------|---------------------------|
| | NiO | MgO | CaO | SiO ₂ | Al ₂ O ₃ | La ₂ O ₃ | CeO ₂ | Other | | | | | |
| Ni aluminate | 45 | | | | 55 | | | | 500-700 in bed | 0.6-0.85 s | Poplar pyrolysis in N ₂ , N ₂ /H ₂ O, CO ₂ , and CO ₂ /H ₂ O | | Arauzo et al. 1994 |
| Ni/Al ₂ O ₃ | 7 | | | | 93 | | | | 800 | | Peat Gasification in N ₂ T= 20-550 @ 5 °C/min | 90.3 | Sutton et al. 2001 |
| Ni/ZrO ₂ | 7 | | | | | | 93% ZrO ₂ | 95.2 | | | | | |
| Ni/TiO ₂ | 7 | | | | | | 93%TiO ₂ | 98.1 | | | | | |
| Ni/SiO ₂ | 7 | | | 93 | | | | 89.7 | | | | | |
| Ni/MOR1 | 7 | | | | | | | 81.9 | | | | | |
| Ni:Al 3:17 | 11 | | | | 89 | | | 91.5 | | | | | |
| Ni:Al 1:3 | 20 | | | | 80 | | | 92.2 | | | | | |
| Ni/olivine | 3.5 | 47 | 0.2 | 39 | 0.1 | | | 0.08 Cr | 600-850 | | CO ₂ /CH ₄ & H ₂ O/CH ₄ | 70-95 | Courson et al. 2000 |
| Ni/Al 3:17 | | | | | | | | | 450-800 | | 5.1 mol%CH ₄ , 18.3 mol% C ₃ H ₈ , 42 mol% H ₂ , 15.5 mol% CO, 19 mol%CO ₂ | 100 | Sutton et al. 2002 |
| Pt/ZrO ₂ | | | | | | | 1 wt% Pt | 90 | | | | | |
| Ru/Al ₂ O ₃ | | | | | 99 | | 1 wt% Ru | 99 | | | | | |
| Ni/Al ₂ O ₃ | 15 | | | | 85 | | | | 825 | 126000 1/h | Poplar bio-oil: aqueous fraction | | Garcia et al. 2000 |
| Ni/MgO-Al ₂ O ₃ | 15 | 8 | | | 77 | | | Mg/Ni=1 | | | | | |
| Ni/MgO-La ₂ O ₃ - Al ₂ O ₃ | 15 | 8 | | | 71 | 6 | | Ni/La=8 | | | | | |
| Ni-Co/ MgO-La ₂ O ₃ - Al ₂ O ₃ | 15 | 8 | | | 68 | 6 | | Ni/Co=3 4 wt% Co | | | | | |
| Ni-Cr/ MgO-La ₂ O ₃ - Al ₂ O ₃ | 15 | 8 | | | 68 | 6 | | Ni/Cr=3 4 wt% Cr | | | | | |
| LaNi _{0.3} Fe _{0.7} O ₃ perskovite | 20 | | | | | | | 43% Fe ₂ O ₃ | 800 | 0.05s | Ar/CH ₄ /H ₂ O/H ₂ and almond shell steam gasification @ 800C with olivine bed | 90 | Rapagna et al. 2002 |
| UdeS = Ni-Cr/ MgO-La ₂ O ₃ - Al ₂ O ₃ | 15 wt% Ni | 10 | | | 65 | 5 | | 5% Cr | 600-850 | 0.55 s or 10080 1/h | steam/naphthalene & biomass gasification @ 750C | 99 | Bangala et al. 1997, 1998 |

| Catalyst (Name) | Composition (wt%) | | | | | | | | Operating Temp (°C) | Space time/ velocity | Feedstock composition | X _{tar} (%) | References | |
|---------------------------------------|-------------------|---|-----|------------------|--------------------------------|--------------------------------|------------------|------------|---------------------|---------------------------------------|---|---------------------------------------|-----------------------|------------------------|
| | NiO | MgO | CaO | SiO ₂ | Al ₂ O ₃ | La ₂ O ₃ | CeO ₂ | Other | | | | | | |
| Rh/CeO ₂ | | 1.2x10 ⁻⁴ mol metal/g catalyst | | | | | | 98 | 1.2% Rh | | | Cellulose gasification in air at 550C | 100 | Asadullah et al. 2001a |
| Ru/ CeO ₂ | | | | | | | | 98 | 1.2% Ru | | | | | |
| Pd/ CeO ₂ | | | | | | | | 98 | 1.2% Pd | | | | | |
| Pt/ CeO ₂ | | | | | | | | 98 | 2% Pt | | | | | |
| Ni/ CeO ₂ | 1 | | | | | | | 99 | | | | | | |
| Rh/CeO ₂ | | | | | | 98 | | | | | 100 | Asadullah et al. 2001b | | |
| Rh/ZrO ₂ (98%) | | | | | | | 1.2 wt% Rh | 450-550 | | Cellulose gasification in air at 550C | 98 | | | |
| Rh/Al ₂ O ₃ | | | | 98 | | | | | | | 98 | | | |
| Rh/TiO ₂ (98%) | | | | | | | 1.2 wt% Rh | 450-550 | | Cellulose gasification in air at 550C | 84 | Asadullah et al. 2001b | | |
| Rh/MgO | | 98 | | | | | | | | | | | | |
| Rh/SiO ₂ | | | 98 | | | | | | | | | | | |
| Rh/CeO ₂ /SiO ₂ | | | | 63 | | | 35 | 1.2 wt% Rh | 500-700 | | Cellulose gasification in air | 86-99 | Asadullah et al. 2002 | |
| Ni-activated filter disks | 0.5-1 | | | | 99 | | | | 750-900 | 0.58-1.39 l/s | 875 ppmv naphthalene in 51% N ₂ , 12% CO, 10% H ₂ , 11% CO ₂ , 11% H ₂ O, 5% CH ₄ | 60-99 | Zhao et al. 2000a,b | |
| Ni/Ca-activated filter disks | 1 | | 0.5 | | 98 | | | | 750-900 | | 4.300 ppmv benzene in 50% N ₂ , 12% CO, 10% H ₂ , 11% CO ₂ , 12% H ₂ O, 5% CH ₄ , 0-100 ppm H ₂ S | 20-99 | Draelants et al. 2001 | |

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