AN OVERVIEW ON CATALYSTS FOR BIOMASS GASIFICATION

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ABSTRACT

Biomass gasification may be a viable alternative to burning fossil fuels directly. Biomass, a CO-neutral renewable fuel source, may help meet demand for heat, power, and 2 synthesis gas. Nevertheless, inefficiencies in the technique make biomass gasification commercially unviable at the moment. Because the resulting gas contains condensable organic molecules including methane, it is inappropriate for some uses. The economic feasibility of biomass gasification will be improved if condensable organic molecules and methane can be removed using a low-cost method. This article includes a comprehensive overview of the three major categories of catalysts that have been tested for the removal of these hydrocarbons. Dolomite, alkali metals, as well as nickel are the three types of catalysts.

KEYWORDS: *Biomass Gasification, Tar, Syngas, Catalysts, Reforming, Dolomite, Alkali Metals and Nickel.*

1. INTRODUCTION

In recent decades, tremendous progress has been made in the design of gasifiers. Gas cleaning, on the other hand, remains a barrier in advanced gas use, limiting the adoption of biomass for power production. The build-up of condensable organic materials in the producing gas, often referred to as tars, may create clogs and corrosion, as well as decrease overall efficiency. Furthermore, the existence of impurities including such methane may influence the syngas' final use, and the methods for removing impurities in these kind of processes are expensive.

Many of the by-products include nitrogen and sulphur, and the equivalent oxides are generated during the burning of the fuel gas; these oxides, NO and SO, may have a detrimental effect on the environment. Catalysis for biomass gasification has piqued people's attention since the mid-1980s. The requirement to generate a tar-free product from the gasification of biomass has fueled progress in this field, since removing tars and reducing methane content improves the economic feasibility of the biomass gasification process. The literature in this field includes anything from bench-scale reactors to plant-scale gasifiers. The development of catalysts for use in the process is often done in conjunction with gasifier design or biomass feed type. The catalyst's requirements, on the other hand, are essentially the same and may be stated as follows:

1.1. The Catalysts Must Be Capable Of Removing Tars:

- If syngas is the intended result, the catalysts must be able to reform methane.

- The catalysts should produce a syngas ratio that is appropriate for the process.

- The catalysts must be resistant to carbon fouling and sintering, which may cause deactivation.

- The catalysts should be replenished quickly.

- The catalysts must be powerful.

- The catalysts must be low-cost.

1.2.Biomass gasification catalysis:

The following sections discuss three different categories of catalyst materials that have been the topic of publications for biomass gasification. Catalysts made of dolomite The Pidgeon method for the thermal reduction of magnesium uses dolomite, a magnesium ore having the general formula MgO PCaCO. Because it is a cheap disposable catalyst that may substantially decrease the tar content of a gasifier's product gas, the use of dolomite as a catalysis in biomass gasification has gotten a lot of interest. It may be employed as a main catalyst, dry-mixed with the biomass, or more frequently, as a guard bed in a downstream reactor. Dolomite's chemical composition varies depending on the source, but it typically includes 30 wt. percent CaO, 21 wt. percent MgO, and 45 wt. percent CO, as well as two trace minerals, SiO, Fe O, and Al O. The surface areas and pore sizes and distributions of the different kinds also vary[1].

1.3.Catalysis with alkali metals and other metals:

Several organizations have looked into alkali metal catalysts for the removal of tar and upgrading of the produced gas. By dry mixing or wet impregnation, the catalysts are often introduced directly to the biomass. The catalyst is difficult to come back when applied this manner, and the gasification process is not always cost efficient. It also increases the amount of ash left behind after char gasification, which is expected to become a disposal issue for the technology in the future years[2].

1.4.Catalysts made of nickel:

Nickel catalysts are the subject of the most important body of literature in the field of hot gas cleaning for biomass gasification. Several organizations have looked into a raw gas cleaning method that includes removing up to 95 percent of the tar using a dolomite or alkali catalyst, then adjusting the gas composition by reforming the methane and residual tar with a nickel steam reforming catalyst. Group VIII metals catalyze steam and dry reforming processes, with nickel being the most frequently utilized among them. As a result, the vast bulk of published research is focused on commercially accessible nickel catalysts for steam reforming of hydrocarbons and methane. When these catalysts are used at temperatures over 740 8C, the hydrogen and carbon monoxide content of the leaving gas is usually increased, while the hydrocarbon and methane content is eliminated or reduced. The methanation process is thermodynamically favorable at lower temperatures, and it is occasionally optimized when methane is wanted as the main component of the leaving gas[3].

Several commercially accessible catalysts for tar removal and product gas composition modification are available. The steam reformation of tar and. methane 2 was studied using two Haldor Topset catalysts, R-67-7H and RKS-1. The catalyst was placed downstream of the gasifier in a secondary w x reactor that's been maintained at temps between 730 and 760 degrees Celsius, with space times of just 0.1 seconds. Catalyst R-67-7H has a Ni concentration of 12–14 percent on a MgrAl O2 3 support with a free Mg content of less than 0.5 wt. percent and a SiO content of -0.2 wt. percent, according to the manufacturer. It had a 12–20 m2 gy1 specific surface area. The decreased catalyst resulted in higher conversions of tar, methane, and C2 and C. The tar

Asian Journal of Research in Social Sciences and Humanities
ISSN: 2249-7315   Vol. 11, Issue 12, December 2021   SJIF 2021 = 8.037
A peer reviewed journal

concentration was decreased to just 4 mg my3 and the methane content was reduced to 0.5 vol. percent. Carbon fouling caused deactivation of the catalysts, resulting in limited catalytic lifetimes. The reduction of tar concentration prior to the nickel catalysts has been discovered as a potential method to keep the catalysts active. A concept employing a guard-bed of dolomite catalyst before the nickel catalyst has also been explored by many authors[4].

TABLE 1: PRODUCTION OF DEFINITE GASES FROM BIOMASS STEAMS GASIFICATION

HARSHAW 326	METHANE RICH	SYNGAS
Gasification T, °C	561 -540	740–770
Catalyst T, °C	550-560	740–760
Steam /wood, /g /g	0.33	0.7
% Carbon to gas	69	90
H_2	29.6	53.1
CO_2	3405	15.5
CO	10.9	28.4
CH_4	25.5	3.2
C_{2+}	0.2	0.1

In both the MR or BSR tests, inactivation was fast when the catalyst was introduced directly to the biomass owing to carbon fouling. The catalysts in the secondary fixed-bed reactor exhibited an early loss of activity in micro-reactor testing, but the activities stabilized after 15–20 hours, with no additional deactivation during a 50-hour test period. After that little time period, the carbon concentration of the catalyst was less than 1 wt.%. The PNL catalyst had just 4% carbon after 1200 hours of exposure in the micro reactor. All catalysts continuing to deactivate throughout the BSR testing. After 16 hours of exposure, the United Catalyst had 6 wt.% carbon[5].

TABLE 1: ILLUSTRATE THE NICKEL CATALYSTS TESTED IN THE TEES PROCESS

PROPERTY	CATALYSTS				
	A	**B**	**C**	**D**	**E**
Types	M	H	H	R	R
Surface area	Moderate	High	High	Low	Low
Nickel	Moderate	High	High	Moderate	Low
Thermal stability	Moderate	Low	Low	Low	High

M =Methanation, H=Hydrogenation, R=Reforming.

Deactivation was caused by nickel metal crystalline development, with carbon fouling identified as the primary result of this crystallite formation. At 700 8C, alumina-supported nickel w x catalysts for steam gasification of wood were tested for durability. Carbon deposition and sintering of the nickel metal particles in the catalyst reduced the catalyst's activity as the gasification time

Asian Journal of Research in Social Sciences and Humanities
ISSN: 2249-7315   Vol. 11, Issue 12, December 2021   SJIF 2021 = 8.037
A peer reviewed journal

increased. At 600. 8C, catalyst renewal was studied under three distinct flows: H, H O, and O. Although the O treatment was claimed to restore the nickel specific area to its original value, transmission electron micrographs of nickel particles in both new and old catalysts clearly exhibited sintering. The presence of carbon in the form of graphite was discovered by XRD analysis of the coked catalyst[6].

Several organizations developed and tested nickel catalysts for removing tars and methane from a gasifier's exhaust gas. The removal of tars from the product gas of a wood pyrolysis unit operating at 650 8C and atmospheric pressure was investigated using a co-precipitated nickel–alumina catalyst with a molar ratio of 1:2. The catalyst was calcined at three distinct temperatures: 650 degrees Celsius, 750 degrees Celsius, and 850 degrees Celsius. They found that a two-hour catalyst reduction period yielded lower tar yields and greater gas yields than a one-hour catalyst reduction time. For catalysts that had been lowered for two hours, the H:CO ratio was two times greater. The tar conversion was found to be affected by the various calcination temperatures of the produced catalyst. Greater tar conversion was coupled by higher gas outputs at lower calcination temperatures[7], [8].

2. LITERATURE REVIEW

Abu El-Rub et al. investigated A project is underway to create a tar removal method downstream of a gasifier that makes use of inexpensive and active catalysts. Catalyst screening was done in a fixed-bed tubular reactor in the initial stage of the research. The method will be designed using the findings of the fixed-bed tests. This article provides an overview of the different kinds of catalysts that have been utilized to decrease tars in producer gas produced from the biomass gasification process in numerous research studies. Mineral and synthetic catalysts are split into two categories based on their manufacturing technique. A summary of the review is also given, as well as suggestions for excellent catalyst candidates for further research[9].

Hydrogen generation via catalytic gasification in supercritical water (SCW) is a potential method to use biomass resources, according to Hui Zhao et al. Supercritical water not only offers a homogenous and fast reaction environment for biomass gasification, but it also creates difficulties with catalyst agglomeration. The supercritical water synthesis technique was used and the preparation process was studied in order to produce active and selective catalyst for biomass gasification in supercritical conditions. Metal elements such as Ni, Co, Zn, and Cu were loaded onto TiO_2 particles, which were shown to be hydrothermally stable in supercritical water. And nanoparticles were created effectively. Metal catalysts have a homogeneous spherical shape with a diameter of approximately 30 nm, according to gas chromatography/mass spectrometer (GC/MS), scanning electron microscopy, energy dispersive spectrometer (EDS), and X-ray diffraction analytical techniques. Metal catalysts made using the supercritical hydrothermal technique have some catalytic properties. The Ni catalyst had the greatest stability, whereas the Zn catalyst had the maximum hydrogen production[10].

3. DISCUSSION

Gasification of biomass may be a feasible alternative to directly burning fossil fuels. Biomass, a CO-neutral and environmentally friendly energy source, may assist satisfy demand for heat, power, and 2 synthesis gas. However, due to inefficiencies in the technique, biomass gasification is now uneconomical. Certain applications are incompatible with the produced gas because it includes condensable organic chemicals including methane. Wet impregnation or dry mixing of alkali catalysts directly into the biomass reduces tar content while also lowering the methane concentration of the resultant gas. These catalysts significantly enhance the rate of gasification when used directly. The catalyst, on the other hand, is difficult and expensive to recover. High quantities of alkali metals are found in the ash of many biomass species. When combined with

Asian Journal of Research in Social Sciences and Humanities
ISSN: 2249-7315   Vol. 11, Issue 12, December 2021   SJIF 2021 = 8.037
A peer reviewed journal

biomass, ash acts as a catalyst for the elimination of tar. Particle agglomeration occurs when alkali catalysts are immediately introduced to biomass in a fluidized-bed gasifier. Secondary catalysts made of alkali metals are also useful. Although not as active as nickel, potassium bicarbonate supported on alumina is more resistant to carbon deposition. Because hydrocarbon conversion seldom surpasses 80%, the catalyst is not appropriate as a secondary catalyst.

4. CONCLUSION

Dolomite is an effective catalyst for removing hydrocarbons produced during biomass gasification. Dolomites boost gas production while lowering liquid product yields. Using the right ratios of biomass feed to oxidant, tars may be eliminated nearly completely. Carbon deposition and wear cause the dolomite catalyst to deactivate; nevertheless, dolomite is inexpensive and easy to replenish. If the catalyst is calcined and put downstream of the gasifier in a fluidised-bed at temperatures over 800 8C, it will be most active. With carbon dioxide, the reforming process of tars over dolomite is faster than with steam. Pore size and distribution are closely linked to dolomite action. When large quantities of iron oxide are present, there is also a greater level of activity. Dolomites are not active in reforming the methane contained in the product gas, thus they are ineffective as syngas catalysts. Dolomite's primary purpose is to serve as a guard bed for heavy hydrocarbons to be removed prior to the reforming of lighter hydrocarbons to create a syngas-quality product gas.

Nickel reforming catalysts that are commercially available are very effective at removing hydrocarbons and adjusting the gas composition to syngas grade. Nickel catalysts work best as secondary catalysts in a downstream reactor that can function under circumstances other than those of the gasifier. When operated at 780 8C in a fluidized-bed reactor, the catalysts are most active and have a longer lifespan. The catalysts may generate a methane-rich gas when operated at cooler temperatures (600. 8C). The catalysts' activity is affected by nickel loading as well as metal dispersion. Carbon deposition as well as nickel particle growth are the main causes of deactivation. The use of a dolomite guard bed may help to minimize deactivation caused to coking. Carbon deposition may also be reduced by adding dopants like lanthanum. Catalysts are efficient, commercially accessible, and reasonably priced.

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Asian Journal of Research in Social Sciences and Humanities
ISSN: 2249-7315   Vol. 11, Issue 12, December 2021   SJIF 2021 = 8.037
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