

A Review on Biomass Tar Formation and Catalytic Cracking

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Abstract. In this paper the path of tar formation during biomass pyrolysis or gasification is described. When the reaction temperature is in the range of 800-900°C, the tar yield is between 2.5% -5%. Meantime, the primary tar approaches 0, the secondary tar content is 40-60%, the tertiary tar content is 20-60%; furthermore, the catalytic cracking of tar and calcined dolomite have some catalytic cracking ability to tar, and the disadvantages of mechanical strength and low anti-wear performance are poor; Nickel-based catalyst has high catalytic activity for tar and the tar removal rate is as high as 99%. A variety of alkali carbonate mixture of tar on the catalytic activity better than a single effect. In the actual application process, the choice of tar cracking catalyst depends on the pyrolysis or gasification of raw materials, treatment processes, reaction temperature and other factors considered.

Introduction

With the rapid economic growth, the demand for energy in our country is increasing day by day. At present, the fossil fuels are in short supply and environmental pollution is grim. The developing renewable and green sustainable energy is a major issue to be solved urgently in the energy field. China's biomass resources are abundant. In 2016, the total available biological resources in China amounted to 945 million tons, equivalent to 460 million tons of standard coal. And about 900 million tons of biomass were not effectively utilized, equivalent to 438 million tons of standard coal, resulting in a large number of resources waste, huge potential for development.

The utilization of biomass mainly adopts the thermochemical conversion method (pyrolysis or gasification). That is, the organic component undergoes thermal decomposition or cleavage reaction such as bond cleavage, isomerization and small molecule polymerization because of being heated and macromolecular organic matter into small molecule syngas, tar and coke process. Pyrolysis refers to the process of "thermal decomposition or cracking" reaction when the air content is zero, and gasification is the process of adding gasification medium and reacting with the organic components[1].

Tar definition, formation and harm

Tar definition. Tar is a complex mixture of ingredients, containing a variety of chain hydrocarbons, cyclic hydrocarbons, aromatic hydrocarbons and heterocyclic organic matter. The tar composition produced by pyrolysis or gasification of different organic materials is not the same. Tar is restricting the pyrolysis or gasification technology to promote an important reason. At the IEA meeting in Brussels, tar was defined as all organic matter boiling above benzene (boiling point 80.1°C)[2]. At the 1998 meeting of the European/IEA/DOE Tar Testing Agreement, many experts favored the definition of tar as all organic pollutants with a molecular weight greater than benzene [3].

Formation. Biomass pyrolysis/gasification contains hundreds of different types of compounds of different nature. The yield and composition of tar depends on the type and nature of biomass feedstock (including size, moisture content, etc.), pyrolysis/gas conditions (temperature, pressure, residence time, etc.), the type of reactor, and other factors.

When biomass is heated, its molecular bonds break down and the resulting small molecule is gas, while the larger molecule is called primary tar. These primary tars are generally fragments of the raw biomass feedstock structure. Primary tars are not stable at pyrolysis / gasification temperatures but react further to form secondary tars. If the temperature rises further, a tar will be converted to tertiary tar [4].

Elliott proposed the following tar formation and pathways: Oxygenated mixtures (400°C)→Phenylether ethers (500°C)→Alkylphenols (600°C)→Heterocyclic ethers (700°C)→PAHs (800°C)→Higher molecular weight PAHs(900°C) using the corresponding tar fractions for each temperature range analyzed by GC/MC (Table 1).

Table 1 Chemical Components in Biomass Tar

Conventional flash pyrolysis (450-550°C)	High-temperature flash pyrolysis (600-650°C)	Conventional steam gasification (700-800°C)	High-temperature steam gasification (900-1000°C)
acids	benzenes	naphthalenes	naphthalene
aldehydes	phenols	acenaphthylenes	acenaphthylenes
ketones	catechols	fluorenes	phenanthrenes
furans	naphthalenes	phenanthrenes	fluoranthene
alcohols	biphenyls	benzaldehydes	pyrene
Complex oxygenates	phenanthrenes	phenols	acephenanthrylene
phenols	benzofurans	naphthofurans	benzanthracenes
guaiacols	benzaldehydes	benzanthracenes	benzopyrenes
syringols			226 MW PAHs
Complex phenols			276 MW PAHs

Evans and Milne[5] used molecular mass spectrometry (MBMS) to study the main constituents of tar obtained at different reaction temperatures and concluded that the primary tar contains cellulose such as levoglucose, glycolaldehyde, furfural, hemicellulose lysate And methoxyphenol

and other lignin lysates as the representative of secondary tar mainly phenols and olefins, tertiary tar mainly aromatic methyl derivatives, such as methylnaphthalene, toluene and indene, etc., three grade tar mainly non-substituted PAH (polycyclic aromatic hydrocarbons) substances, such as benzene, naphthalene, acenaphthene, anthracene, pyrene and phenanthrene.

The distribution of the four components in the tar is shown in Fig. 1. When the tertiary tar is present (700~800°C), the primary tar has disappeared. When the temperature reaches 1000°C, the secondary tar and the tertiary tar also close to disappear, leaving only concentrated three tar PAH; this time the total amount of tar is already very small, but the PAH need to be pyrolyzed at higher temperatures.

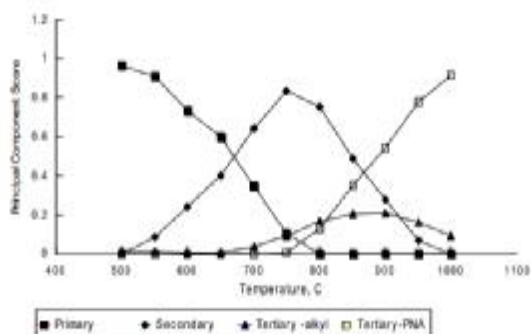


Fig.1 Distribution of tar four components

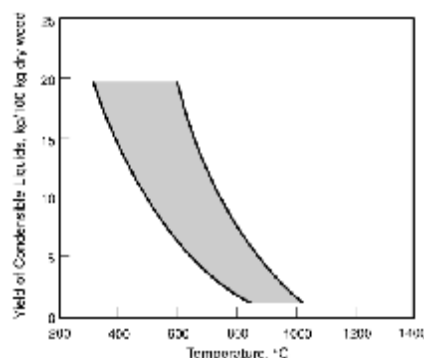


Fig. 2 Relation of tar and the reaction temperature

Baker [6] et al. The amount of wood tar on the aspirated and aspirated gasifiers is 12% and less than 1%, respectively, of the feedstock, the amount of tar produced in the steam gasification fluidized bed gasifier at 600°C and 750°C is 15% and 4%, and the relationship between the amount of tar and the reaction temperature is obtained as shown in Fig. 2. From Fig. 1 and Fig. 2, it can be seen that the most suitable temperature range for biomass pyrolysis or gasification is 800-900°C and the tar yield is between 2.5% -5%. At this time, the primary tar approaches 0, the secondary tar content 40-60%, tertiary tar 20-60%.

Disadvantage. The presence of tar reduces the efficiency of cold gas in pyrolysis/gasification. The energy of the tar product typically ranges from 5% to 15% of the total energy, which is difficult to utilize with combustible gases at low temperatures. Tar exists in the gas product, which will gradually condense during the process of conveying in the pipeline to form a viscous liquid substance, which adheres to the inner wall of the pipeline and the wall of the relevant equipment, posing a threat to the safe operation of the equipment. At the same time, the tar also contains toxic and harmful substances such as phenol, aldehyde, formaldehyde and higher levels of polycyclic aromatic hydrocarbons, which not only endanger human health but also lead to serious environmental pollution.

Tar removal technology

Physical method. Tar removal method can be roughly divided into physical and thermal chemical method of two categories, there are more methods of physical removal of coke wet, dry and electric tar picker at present. Wet method is divided into spray method and bubbling method, the use of water to remove the tar in the gas phase products, adding a small amount of alkali can make the purification effect has improved. The most common type of wet scrubber is the spray tower. The atomizing spout is arranged in multiple rows within the tower. The gas, after being sprayed down the rows, removes the tar and dust from it. Dry method, also known as filtration method, use multi-stage filtration purification method, the highly adsorbable material installed in the container, so that the fuel gas containing tar through the adsorbent material and tar filtered out. Electric tar

picker can remove 99% dust and 40-70% tar, electric capture tar, the gas contained in the heavy oil is completely removed.

Thermochemical method. Thermochemical method includes two kinds, one is thermal cracking, the other is catalytic cracking. Pyrolysis is the initial synthesis gas heating, the common method is to add a small amount of hot gas in the air, so that part of the combustion and increase the temperature. There are two directions for the tar's reaction path. Some of the tar is cracked into light gas and the other part is converted to polycyclic aromatic hydrocarbons (PAHs) that are difficult to pyrolyze. Water vapor is generated as the tar is converted.

Catalytic cracking is the initial synthesis gas flowing through the catalyst surface at a temperature, the tar molecules split into light gas, accompanied by the production of a certain amount of carbon black process. Because of the catalyst, the activation energy required for tar cracking is greatly reduced, enabling tar conversion at lower temperatures and higher tar conversion efficiency. As a highly efficient tar conversion method, catalytic cracking has become one of the research directions of biomass pyrolysis gasification technology.

Research Status of Tar Catalytic Cracking

Excellent catalyst should have these characteristics, these features are effective tar removal, strong anti-carbon deposition capacity, effectively regulate the composition of syngas, good anti-sintering anti-wear performance, low price. In tar catalytic cracking, a number of materials have been studied, including many natural minerals, metals and charcoal. For example, limestone, dolomite, olivine, magnesite, alkali metals and the like. Catalysts fall into three categories: ore-based catalysts, alkali metal catalysts and nickel-based catalysts. In recent years, pyrolysis gasification also used some new catalysts, such as charcoal and biomass coke.

Dolomite. Dolomite is a mixture of calcium carbonate and magnesium carbonate. The molecular formula is generally written as $\text{CaMg}(\text{CO}_3)_2$. After calcination, MgO containing about 30% (mass fraction) CaO about 20% (mass fraction) and SiO_2 , Fe_2O_3 , Al_2O_3 and the like are contained. Most studies suggest that carbonate catalysts such as dolomite and limestone have higher catalytic activity only after calcination. Studies by Simell et al.[7] show that the partial pressure of CO_2 in the pyrolysis reaction cannot be higher than the equilibrium decomposition pressure of CaCO_3 . Dolomite catalyst in the gasifier, the tar removal rate of 80% or less, used in the downstream secondary reactor, the tar reduction rate can reach 95%. With dolomite cracking catalyst, it is difficult to achieve 90% to 95% of the tar conversion rate, or gas tar content of less than $500 \sim 1000 \text{ mg/m}^3$. Dolomites are more likely to catalyze the cleavage of primary and secondary tars (such as phenols and their derivatives), while polycyclic aromatics such as naphthalene and indene are more difficult.

He et al [8] on the downstream fixed bed reactor calcined dolomite catalytic cracking of tar, the amount of garbage to feed 0.257 kg/h , water vapor flow of 0.198 kg/h , the gasification temperature of 900°C , In the absence of steam and catalyst, the tar content was 38.54 wt%; Access to water vapor and do not add the catalyst, the tar content of 0.23wt%; When steam is added and the catalyst is added, the tar content is zero.

Nickel-based catalyst. Nickel-based catalysts are widely used in naphtha and methane reforming in the petrochemical industry, and a large number of nickel-based catalysts are commercially utilized. Zhang [9] studied the tar removal rate in a tar conversion system consisting of a guard bed and a catalytic reactor. Three nickel-based nickel-based catalysts (ICI46-1, Z409 and RZ409) proved effective in removing heavy tar In addition to $> 99\%$, hydrogen production increased 6-11 vol% (dry basis). Experimental results show that the gas velocity has little effect on the gas composition, while

increasing the temperature can increase hydrogen production and reduce the amount of light hydrocarbons (CH_4 and C_2H_4). Coll [10] studied the cleavage of model compounds such as benzene, toluene, naphthalene, anthracene and pyrene by two commercial nickel-based catalysts, 700-800°C: UCG90-C and ICI46-I. The reactivity of these tar model compounds was benzene>toluene>anthracene>pyrene>naphthalene. The ICI46-I catalyzed toluene conversion was 40-80% and UCG90-C catalyst conversion was 20-60%.

Nickel-based catalysts have a better pyrolysis efficiency than charcoal and dolomite and achieve complete conversion of tar and methane but are more sensitive to gas composition. For example, a small amount of sulfur in gas may cause catalyst poisoning, and the product of tar conversion Carbon also quickly deactivates the catalyst.

Alkali metal catalyst. Alkaline metal catalysts, also known as natural catalysts, contain a small amount of basic metal species in biomass and many wastes and catalyze the thermochemical conversion of all forms of biomass. Gong [11] studied the gasification of waste paper using a molten alkali metal carbonate containing a mixture of potassium, sodium, and lithium carbonate as a catalyst to accelerate ($\text{C} + \text{CO}_2 = 2\text{CO}$) the molten catalyst, The experimental results show that the mixture of several carbonates enhances the catalytic ability of the catalyst more than any single carbonic acid. Demirba [12] studied the non-catalytic pyrolysis and catalytic pyrolysis characteristics of cotton cocoons, tea plants and olive shells, obtained hydrogen-rich gas at 775K, 925K, 975K and 1025K, In the catalytic pyrolysis process with the use of ZnCl_2 catalyst, although the coke and liquid products have increased, the amount of hydrogen gas production also increased; The effect of K_2CO_3 and Na_2CO_3 on the pyrolysis products depends on the biomass type.

Charcoal and biomass coke. Charcoal is also a studied tar conversion material. Due to its large porosity and specific surface area, as well as a certain amount of alkali ash in the ash, it has a good catalytic effect on tar cracking. Studies have shown that coke and biomass coke at 950°C, residence time 0.5s, tar removal rate can reach 100%, however, it may be consumed by water vapor or syngas in the CO_2 .

Li [13] used quartz sand as a reference to study the effects of semi-coke removal on tar in a fixed bed. Compared with quartz sand, the pyrolysis tar yield of semi-coke is reduced and the tar gasification light oil component is increased. The catalytic effect of semi-coke is related to its physical properties and inorganic substances, which have a greater impact than the former.

Conclusion

In the biomass pyrolysis or gasification process, tar yield composition depends on the type and nature of the biomass feedstock, the pyrolysis/gasification conditions, the type of reactor, and other factors. In the process of tar formation, the most suitable temperature for biomass pyrolysis/gasification is 800-900°C, and the tar yield is between 2.5% -5%. At this time, the primary tar approaches 0, the secondary tar content 40- 60%, three levels of tar 20-60%. For the catalytic cracking of tar, although dolomite is cheap, the tar has some catalytic cracking activity, but its mechanical strength is low and its wear resistance is poor. Nickel-based catalyst has high catalytic activity for tar, tar removal rate as high as 99%; The catalytic activity of a mixture of a plurality of alkali metal carbonates on tar is higher than the catalytic activity of a single alkali metal carbonate, the catalytic activity of the same alkali metal carbonate for different biomass tar depends on the type of biomass; Charcoal and biomass coke at 950°C, residence time 0.5s, tar removal rate can reach 100%, however, it may be water vapor or syngas in the consumption of CO_2 . Overall, each catalyst has its own advantages and disadvantages, in the actual application process which as the tar cracking catalyst depends on the pyrolysis or gasification of raw materials, treatment processes,

reaction temperature and other factors considered.

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