

Review of Various Treatment Technologies for Different Waste Streams of Small Scale Gasification System

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Abstract - In today's energy scenario, gasification seems to be an effective utilization of the fossil fuel like coal or biowaste. Though many developed technologies available for the gasifier manufacturing; there is an unresolved question of proper handling of the waste streams generated from the gasification system from environment point of view. Here in this paper it has been tried to cover many treatment technologies or alternates for these waste streams generated from the system. Gaseous emissions can be controlled by using absorption and flare system. Tar having high calorific value can be substituted as an alternate fuel for heat generation. Ash or soot can have many alternate beneficial uses and liquid waste stream can be treated with series of biological or physiochemical treatments.

Keywords - Waste stream of Gasification, Tar, Liquid effluent, Ash, Emission, Treatment technology.

I. INTRODUCTION

Gasification is a process of partial combustion and reduction which converts combustible carbonaceous material into Gaseous fuel. It is a thermo chemical conversion of hydrocarbon material to gas which is also known as syngas/ producer gas/town gas/ coal gas/ synthetic gas etc. The equipment used for this conversion is known as Gasifier. The produced raw gas from gasifier then converted into other desirable products like hydrogen, ammonia, or other chemicals or it can be used as direct combustion after cleaning or can be used to generate electricity. Rather than burning the coal or any other feedstock directly, gasification offers advantages of high calorific value, low pollution and product flexibility. Based on the feed capacity or the syn-gas production capacity the gasifiers can range from large scale to small scale gasification system. Large scale systems are used for the high product flexibility and having the capacity more than 10 MW th. IGCC (Integrated gasification Combine Cycle) used for co-generation of power, steam, hydrogen and elemental sulphur is one of the example of large scale gasification system. While small scale systems are adopted when there is need of direct thermal applications like drying, heating or low power generation. There are many industrial sectors which use these types of gasifiers for fulfillment of its gaseous fuel need. Many industries like ceramics, cement & lime, textile process, paper & pulp are using syn gas as a fuel for their furnace, kiln, dryer, incinerator, hot air generator etc and adopting gasifier for syn gas production. The simple flow diagram for the small scale gasification system is as per figure 1.

When feed stock (generally coal or biomass) is reduced to gaseous form is said to be raw gas (having composition of CO, H₂, CO₂, H₂O, H₂S, CH₄, ash, etc) which must be cleaned and cooled prior to further application. This cleaning process include cyclone or air bag filter for removing ash, water scrubber or ESP, direct or indirect water cooling system. As a result of the whole gasification processes following waste streams are generated.

- Solid waste stream (Unburned feed stock/ ash/soot)
- Liquid waste stream (Black liquer type effluent)
- Semi solid waste stream (Tar)
- Gaeous emissions.(Furnace exit/ gasifier exit gases)

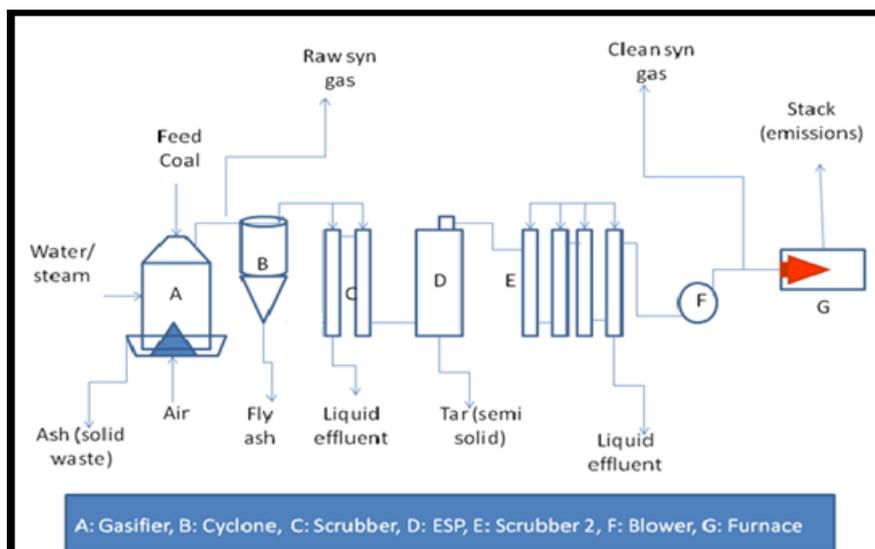


Figure:1 Schematics of small scale gasification system

II. LITERATURE REVIEW

Here in this paper the various feasible methods to treat all the above mentioned waste streams are discussed thereof.

Solid waste stream (Unburned feed stock/ ash/soot) alternates or treatments.

Gasification generates the large quantity of ash, unburned feed, soot etc which ends-up as a dump, so here some interesting alternates or provisions for treatment of that solid waste are discussed.

A. Jonker et al (2005) suggested that most possible application of coal ash is to develop a novel ceramic body, which can potentially be used as a ceramic filter for purification of wastewater and potable water by formulating the different combination with clay, bentonite, gypsum etc to get desired properties. [1]

Fly ash from an Indian thermal power station was characterized by Sen S. K. et al (1997), and used the same for development of wall tiles, acid and abrasion-resistant tiles and sewer pipes. [2]

Koukouzas et al (2010) investigated the possibility to produce high-value zeolitic adsorbents via hydrothermal treatment of coal fly ashes derived from fluidized bed combustors. [3]

Ash particles (with high Ca) have been employed to produce aluminium composites by M. Balsamo et al (2012) This composite has improved mechanical properties and the same can be applied in different sectors including automotive and aerospace. [4]

Coal combustion Ash (CCA) can be considered as a cheaper alternative to the use of activated carbons. M. Balsamo et al (2012) has experimented the gasification treatment of CCA in steam or in carbon dioxide to improve the adsorption property. CCA gasification involves the conversion of the unburnt carbon into gaseous products, and it can be very effective in the development of ash porosity. The beneficiation of a coal combustion ash by either steam or CO₂ gasification was investigated by means of tests on cadmium adsorption. The CO₂ gasified ash appeared as a better Cd²⁺ sorbent than the steam-treated material. [4]

Rbstami H. et al (1996) has found that Chemical Activated Fly-Ash (CAFA) is a new cementitious material, which is used to produce concrete for construction. CAFA can be used to create a variety of concrete strengths and could revolutionize the concrete product manufacturing industry due to its economy. CAFA contains 80-95% Class F fly ash and is used as cement to bind sand, stone, and fibers creating concrete. CAFA concrete has been tested for strength, durability, mechanical properties and, most importantly, was found to be economically and technically viable for many construction applications. Some properties include rapid strength gain (90% of Ultimate in 1 day), high ultimate strengths (16,000 psi in 1 day), excellent acid resistance, and freeze thaw durability. CAFA's resistance to chemical attack, such as sulfuric (H₂SO₄), nitric (HNO₂), hydrochloric (HCl), and organic acids, is far better than Portland cement concrete. Near term applications of CAFA material are, block, pipes, burial vaults, median barriers, sound barriers, and overlaying materials. High strength construction products, bridge beams, pre-stressed members, concrete tanks, highway appurtenances, and other concrete products are targeted as eventual markets. [5]

Yu, Y. et al (1998) treated the Fly ash by acids (1N HCl or 1N H₂SO₄) to form coagulant. The fly ash coagulant displayed better coagulation properties than normal coagulant such as Al₂(SO₄)₃ and FeCl₃. [6]

Liquid waste stream (Black liquor type effluent)

Liquid waste containing phenolic compounds and high TDS as well high ammonical nitrogen presents a serious discharge problem due to their poor biodegradability, high toxicity and ecological aspects. These are the widely present contaminants in the effluents generated from coal tar, plastics, leather, paint, pharmaceutical, steel, textile, timber, paper pulp, insecticides, pesticides and oil refineries. Efficient removal of phenol and its derivatives in aqueous as well as in non-aqueous solution has drawn significant concerns. Here it has been tried to cite many treatments form the field of gasification as well as form other related fields.

Activated carbon, as one of the active adsorbents, has been extensively used in the adsorptive process due to its predominant proportion of micropores. However, its use is limited in application by its high cost, poor mechanical strength, poor adsorption selectivity, and inefficient regeneration. M. Anbia (2009) has found the alternative adsorbents like CMK-1 (ordered mesoporous molecular sieves of Carbon) which can be used as an adsorbent for numerous organic compounds. Their particular properties are

high surface areas, regular frameworks and narrow pore size distributions. These materials have potential application in many fields, such as catalysis, adsorption etc. Ordered mesoporous carbon coated with polyaniline (CMK-1/PANI) shows good adsorption for phenolic compounds. [7]

Z. Wang et al (2012) has developed the unique A2O-MBR system consist of three reactors in series (A1-A2-O MBR), an anaerobic acidification reactor (A1), an anoxic de-nitrification reactor (A2), and an aerobic (organic membrane reactor (O MBR) for the removal of COD, ammonical nitrogen and phenolic compound removal. The removal capacity of each pollutant determined at different Hydraulic Residence Time (HRT) and mixed liquor recycle ratios (R). The experimental results showed that this system could effectively deal with COD and phenol removal and give the same result while the operational parameters altered, but the denitrification was sensitive to operational conditions. The best performance was obtained at HRT of 48 h and R of 3. The maximum removal efficiencies of COD, $\text{NH}_4^+ \text{-N}$ and phenols were 97.4%, 92.8% and 99.7% respectively. [8]

Major amount of phenols and nitrogen compounds from coal gasification wastewater treated with processes of ammonia stripping and solvent extraction of phenol can be reduced for the subsequent biological treatment. However, some emulsified coal tar still exists in the influent and many substances in coal tar are toxic to microorganisms. Z. Wenqi et al (2006) introduced the acidification process of the wastewater by pure hydrochloric acid which can reduce the chemical oxygen demand (COD), total organic carbon (TOC), total phenolics and oil about 3.1%-11.3%, 6%- 10.8%. 5.3%-8.6% and 25.2%-57.4% respectively with pH value in the range of 4 to 7. The analysis of molecular weight distribution indicates that compounds removed from the wastewater by this process are large molecular substances. This treatment can be used as pretreatment with combination of biological treatments. The acid like HCl, H_2SO_4 and H_3PO_4 can be used as an acidification emulsifier agent with additives like kaolin (about 1μ) and diatomite ($3\text{-}50\mu$) which can change the structure of flocs and increase the sedimentation rate at a dosage of 100 mg.L⁻¹. [9]

Nakhla G. F. et al (1995) has studied the anaerobic treatment of coal gasification waste water. Here coal gasification wastewater was treated by the anaerobic reactor operating with periodic anaerobic mass replacement. The system at a COD loading of 4.7 kg/m³ was checked. This treatment is able to achieve over 94% COD removal, more than 99.9% phenol removal, 98-99% cresols removal, and complete removal of di- phenols. [10]

Conventional treatment of CGW includes a series of biological treatment (mostly anoxic-oxic process and activated sludge process) after physio-chemical pretreatment to reduce the concentrations of phenols and ammonium. Although quite effective, these processes are still not enough to meet the strict requirements of the National Discharge Standard. The biologically treated CGW still contains a large number of toxic and refractory compounds as well as their derivatives, with lower biodegradability than the raw wastewater. The biologically pretreated CGW effluent contains large amounts of typical nitrification inhibitors, such as phenols, NHCs and PAHs. A system integrating anoxic moving bed biofilm reactor (ANMBBR) and biological aerated filter (BAF) with short-cut biological nitrogen removal (SBNR) process was investigated by H. Zhuang et al (2014) as an advanced treatment of real biologically treated coal gasification wastewater (CGW). The results proved that the system had efficient capacity of degradation of pollutants especially nitrogen removal. The best performance was obtained at hydraulic residence times of 12 h and nitrite recycling ratios of 200%. The removal efficiencies of COD, total organic carbon (TOC), $\text{NH}_4^+ \text{-N}$, total phenols and total nitrogen (TN) were 74.6%, 70.0%, 85.0%, 92.7% and 72.3%, respectively. [11]

A combined process consisting of a powdered activated carbon technology (PACT) and short-cut biological nitrogen removal reactor (SBNR) was developed by Q. Zhao et al (2013) to enhance the removal efficiency of the total nitrogen (TN) from the effluent of an anaerobic sludge bed (UASB) reactor, which was used to treat coal gasification wastewater (CGW). Powdered activated carbon technology (PACT) was a promising method to remove aromatic compounds. In the shortcut biological nitrogen removal (SBNR) process, ammonia is partially oxidized to nitrite and the nitrite is directly reduced to dinitrogen (N_2). [12]

Sodium dodecyl sulfate (SDS) was employed as an anionic surfactant in the Surfactant-induced coagulation process for the rapid removal of estrogens and phenolic compounds from water by T. Saitoh et al (2014). Here SDS solution is added with Poly solution. Immediately, the resulting solution was vigorously mixed with a rotary shaker for 10 sec to induce the coagulation of PAH-SDS complexes, which can be removed from the surface of water and separated. Combined use of horseradish peroxidase (HRP) and hydrogen peroxide significantly increased the collection yields of the estrogens, because of their HRP-induced oxidation and spontaneous binding to PAH. With the HRP and the hydrogen peroxide concentration of 10 mg/L, nearly complete (>98%) removal of four estrogens was achieved within 10 min at 30°C in the pH region from 6 to 7.5. [13]

M. Irfan et al (2013) have concluded that coagulants used in combinations were found to be more effective in reducing COD, TSS and colour instead of using individual form for the treatment of waste water from pulp and paper industry. There are many coagulants and flocculants like alum, ferric chloride, aluminium chloride, ferrous sulphate, poly aluminium chloride (PAC), cationic and anionic polyacrylamide polymers available in individual form as well as in different combinations. The initial pH of the effluent for coagulation process was found to have remarkable effect on COD, TSS and color removal. Maximum COD, TSS and colour reduction of 16%, 50%, 46% and 13%, 48%, 52% was achieved by using Ferric chloride and Aluminium chloride at their optimum pH. The addition of cationic PAM and anionic PAM was found to be excellent for reduction of COD, TSS and colour at optimum pH value of 2. The reduction in COD, TSS and Colour by PAM cationic and PAM anionic was measured in order of 74%, 93%, 77% and 72%, 93%, 78%, respectively. [14]

Removal of phenolic compounds from rubber-textile wastewaters (RTWWs) investigated by Z. Bas et al (2002) using four different types of coagulants ($\text{Al}_2(\text{SO}_4)_3$, $\text{Fe}_2(\text{SO}_4)_3$, FeSO_4 , FeCl_3) with or without lime ($\text{Ca}(\text{OH})_2$) addition. The optimum results were obtained by using 50% FeCl_3 solution and lime at various dosages at 23 °C, which satisfy the decision criterion of high treatment efficiency (TE) in removing the phenolic compounds, good settling rate (SR) of the flocs, and a reasonably low cost of treatment. [15]

Wastewater from textile dyeing and finishing industries is a significant source of environmental pollution in terms of colour and TOC content. M.N. Pons et al (2005) have found an electro-coagulation as an efficient process, even at high pH, for the removal of

colour and total organic carbon in reactive dyes textile wastewater. The efficiency of the process is influenced strongly by the current passed and the residence time of the reaction. [16]

Semi solid waste stream (Tar) treatments

Tar formation and its solution remains an unsolved problem in most of the coal, biomass and agricultural waste gasification processes. It is important to take the glimpses of relative tar treatment available.

Catalytic tar gasification with steam seems to be attractive because tar has very high calorific value. The enhanced fuel-gas formation that results from the addition of a tar gasification step would contribute to the process efficiency. N. A. Alarcon et al (1999) has studied the tar gasification to yield the gaseous products like H₂, CH₄ and CO at 7200 C. The higher yield obtained during pyrolysis of the Petrox tar. [3.45] The reactivity of the tars can be assessed by comparison of the minimum steam to tar ratio RV_{min} required for 90% conversion. [17]

Tar content of the product gases from gasification of carbon component is important factor influencing the subsequent process steps. The tar evolution profile of main tar constituents were obtained during 1 hr gasification run of coal in a pressurized fluidized bed at 700-9000C and 0.4 MPa by G. Chen et al (2000). The analysis showed that the constituents of the Tar decreases with increase in run time. Rise in temperature leads to progressively increase of aromatics at the expense of phenols and toluene. [18]

The Guo Y et al (1996) investigated the separation of poly aromatic hydrocarbons from coal tar. They searched that 2 and 3 fused-ring aromatics such as naphthalene, methylnaphthalenes, biphenyl, dimethylnaphthalenes, dibenzofuran, fluorene and anthracene can be selectively extracted with methanol and ethanol from coal tar. [19]

The process for converting coal tar into light oil includes thermal cracking, catalytic cracking, and hydro cracking. Kawase M. et al (2003) studied the thermal cracking of coal tar. Thermal Cracking converts coal tar under heating conditions at reaction temperatures up to 10000C. The main reaction involved is condensation, which has a high coking rate of 80%. As a result, the thermal cracking process shows low selectivity for light oil production. [20]

Dou B.L. et al (2008) reviewed the catalytic cracking of coal tar. It converts coal tar under heating conditions with the addition of catalyst. Its reaction temperature is as low as about 5000C and the coking rate is also rather low when compared with that in the thermal cracking process. Ni–Mo is the effective active metal system loaded on a Y zeolite support in the catalytic cracking process, and noble metal Pt and Pd are highly active for the hydrogenation of aromatics. [21]

The process of hydro cracking of coal tar has been investigated by J. Wang et al (2012). The process employs a catalyst and hydrogen to crack coal tar at reaction temperatures as low as 350–4000C and operating pressures of 12.5–20.0 MPa. The catalytic cracking reaction and hydrogenation involved in the hydro cracking process result in a high liquid product yield. They proposed that Y zeolite catalyst has been found to show high hydrogenation and cracking activity and to effectively improve the yield of light oil from coal tar hydro cracking. Ni–Mo–Pd–Y zeolite catalyst, prepared by loading Ni–Mo and Pd metal onto Y zeolite, is expected to show high activity in the coal tar hydro cracking process. [22]

J. Wang et al (2012) have studied the super critical hydrocracking process. It employs a super critical solvent and hydrogen to crack coal tar. Gasoline is more suitable for supercritical solvent in coal tar hydro cracking, and the maximum yield of light oil from HTCT (high temperature coal tar) and LTCT (low temperature coal tar) hydro cracking were obtained at gasoline solvent to coal tar ratio 2:1 and 1:1, respectively. The optimal operating parameters are temperature 3800C, hydrogen pressure 2.0 MPa, gasoline solvent to coal tar ratio 2:1, residence time 20 min, and 8% catalyst to obtain the maximum yield of light oil from the HTCT hydrocracking process has been reported. [22]

Several catalysts were tried by Velegol, D. et al (1997) for catalytic cracking of coal tar, and finally it was found that Linde LZ-Y82 zeolite was the most effective catalyst tested for tar conversion to coke and gases. It also converts the sulfur compounds of the tar into hydrogen sulfide. LZ-Y82 cracked most effectively in the temperature range 500-530°C. [23]

Gaseous emissions (Furnace exit/ gasifier exit gases) treatments

When syngas generated by gasification is being used in the combustion section it creates some gaseous pollutants (flue gas) sometimes exceeding the permissible limits more or less depending on the quality of feed of gasification or syngas composition. Thus flue gas must be treated before it released to the atmosphere.

Guo et al (2001) found that activated carbon prepared from oil palm stone has the ability to remove NO₂ through adsorption of flue gas. These oil palm stones are major solid wastes generated from palm-oil processing mills. [24]

Radlein D. et al (1999) studied the effect of adding the NO_x removing agent. Nitrogen oxides removing agents are the reaction product of a carbon compound and a nitrogen compound such as ammonia, ammonium hydroxide or urea. The carbon compound is selected from carboxylic acids, phenols, esters, aldehydes and ketones. This agent can be either introduced in the NO_x contaminating flue gas or in the fuel to be combusted (syngas). [25]

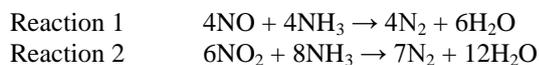
F.W. Vander et al (1981) have investigated the new technique for thermal NO_x removal. In the proposed technique the ammonia is injected into the hot flue gases where the temperature is between 900 and 1000°C. The mixing of ammonia and flue gases must be very fast. In actual performance the NO-removal is found about 50% at a NH₃-NO stoichiometric ratio of one. The thermal De-NO_x process is based on the non-catalytic reaction between NH₃ and NO in the temperature range from 900-1000°C: [26]



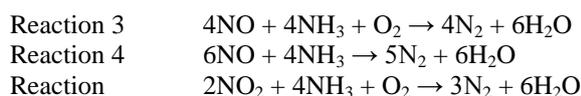
Activated carbon can act as a catalyst for the reaction between NH₃ and NO at the relatively low temperature of 220oC. This fact, and the ability of the activated carbon to absorb SO₂ from the flue gases, has led to a proposal for a system for the

simultaneous removal of NO and SO₂ from the flue gas. Another possibility for the simultaneous removal of SO₂ and NO_x is the CuO- catalyzed process. SO₂ is absorbed on CuO at about 4000C. [26]

Bilitewski B (1997) studied and compared both catalytic and non catalytic NO_x removal processes. They employed NH₃ or Urea for selective non catalytic reduction (SNCR) of NO_x and air as a catalyst with NH₃ or Urea for selective catalytic reduction (SCR) of NO_x. SNCR applies dry urea (CO (NH₂)₂) or ammonia (NH₃) as reductive agents directly in the furnace. At temperatures between 900 and 1050°C the reducing agents react with the nitrogen oxides to form water and nitrogen (Equations 1 and 2). [27]



In SCR the reductive process takes place in a catalyst, where at temperatures between 200 and 400°C a mixture of ammonia and air reacts with the flue gas to form oxygen and water (Equation 3, 4 and 5). The SCR module must be installed after the particulate material and acidic gases are removed. SNCR can achieve reduction rates of 70 percent while SCR can achieve up to 85 percent. [27]



III. SUMMARY

Development of new process technologies for the treatment of all waste streams of coal gasification system is the main objective of the current research studies. It also has lots of commercial significance. Due to involvement of government authorities related to environment safety, now a day it becomes very crucial to bring all these waste stream composition up to the dischargeable limits specified by the respective regularities. Due to extreme high composition of contaminants present in the liquid waste stream, it becomes a major challenge to treat. Literature survey suggests that there are many treatments available for all these streams but proper understanding of the system and the application in the right way is more important for efficient control. Further efforts and understanding is required to reduce all these contaminants up to acceptable level and replace the traditional process of cleaning.

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