

A Review on Developments in Catalytic Filters for Production of Bio-Syngas As Green Fuel

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Abstract: Bio-syngas is a renewable fuel produced by thermochemical conversion of waste biomass and agricultural residues. It contains tar and other particulate matters, so it should be cleaned before its use as green fuel. This paper provides an overview of bio-syngas cleaning technologies, including particle removal systems, catalysts, and the recent development of catalysts to remove tar from the bio-syngas. Nickel is a widely accepted catalyst, but metallic based catalysts make the filter costly and causes rapid deactivation. Activated char catalysts have higher catalytic performance and less harmful to the environment, but exhausts rapidly. Promoters can be used in the catalyst compositions to reduce coke formation and increase activity time for active catalysts. A good catalyst should have high tar conversion efficiency, be inexpensive, easy to regenerate, and environment friendly. To make the filter compact, both the processes of filtration and tar conversion should be combined into one step process.

Keywords: Bio-syngas, Biomass, Filter, Catalyst, Char, Tar, Particulate

I. INTRODUCTION

Fossil fuels including oil, natural gases and coal are currently in verge of being extinct and also polluting the environment. The demand for energy is continuously increasing due to the increasing growth of the world's population, which has led to the depletion of fossil fuel sources. Therefore, many researchers have been focusing on renewable sources of energy in order to replace conventional fossil fuels. The renewable sources of energy include biomass, solar, wind, etc. The biomass can be converted into useful and clean fuel by thermochemical conversion process like gasification. Biomass includes wood, wood residues, agricultural residues, industrial wastes etc. Gasification of biomass converts the biomass into gaseous fuel, which can be used for power generation through gas turbines, internal combustion (IC) engines, and thermal applications [1]. The bio-syngas is a mixture of hydrogen (H₂), methane (CH₄), carbon dioxide (CO₂), carbon monoxide (CO), and water vapors. After gasification of biomass, the bio-syngas has several impurities. The impurities are particulate matters, condensable hydrocarbons (tars), nitrogen compounds (NH₃), alkali metals, hydrogen chloride (HCl), and sulphur compounds (H₂S and SO₂) present in bio-syngas [2]. The particulate matter consists of the dust, soot, ash, char and the tars in the bio-syngas consisting of toluene, naphthalene, benzene and heavy aromatics. Tar is defined as "The organics, formed during gasification of any organic substance" and is typically aromatic compound.

II. SYNGAS CLEANING SYSTEMS

Syngas produced after gasification of biomass comes out in raw syngas which contains gas, char particles, ash particles and tar. This raw syngas is required to be cleaned. Some of the cleaning systems like cyclone separators, rotation particle separators, sand bed filters are found in literature. To remove particles from the gas stream, cyclones, apply centrifugal force on the particles [3]. This is accomplished by steering the flow of gas in a circular direction due to the inertia that the particles are unable to follow. The cyclone separator for gas cleaning is good enough to remove the particulates compared to the tars [4]. [5] performed the test on the rotation particle separator to remove the particulates from the gas. Both liquid and solid particles can be removed from the gas. The test resulted up to 100% separation efficiency for particles size of diameter 0.1 μm and above.

[6] performed the test on a venture scrubber, sand bed filter, wet electrostatic precipitator, fabric filters, and a rotational particle separator (RPS). It was reported that the tar separation efficiency for RPS and Fabric filter were 30-70% and 0-50% respectively. The removal of particulates in gas was more effective than the tar removal in the RPS. It was mentioned in their paper that alone RPS or fabric filter are not effective to remove the tars significantly from the gas.

III. METHODS FOR TAR REMOVAL

The particles and tars are the most significant contaminants that need to be removed. If not, the tars may condense and cause blockage, which clogs engines, filters and lines. The particulates may also affect the environment and degrade metallic components. There are several advanced alternatives that promise to significantly minimize the quantity of tar. However, the technique must be effective in removing tar, economically viable, and most significantly, it must not interfere with the production of beneficial gaseous products. Depending on where the tar is removed, all possible methods may be divided into two categories: those (i) used inside the gasifier itself (referred to as the primary method) and (ii) used outside the gasifier (referred to as the secondary method).

A. Primary methods for tar removal

The Primary method for tar removal should be ideal which may eliminate the use of the secondary method. In primary method, tar is cleaned inside the gasifier (Fig. 1). The three main problems are (1) choosing right operating parameter and conditions of gasification, (2) using the right bed additives or catalysts, and (3) choosing the suitable design of gasifier.

Primary measures may be important for the gasification process, but they cannot achieve the goal of tar elimination without changing the usable composition of gas and its heating value. The reduction of tar using downstream gas cleaning techniques is said to be quite effective. Combining appropriate primary measurements with downstream techniques is proven to be highly beneficial in every way [7-8]. With a focus on the catalytic conversion of tars, the literature on the secondary treatment for the tar conversion and particulate removal from bio-syngas needs more analysis.

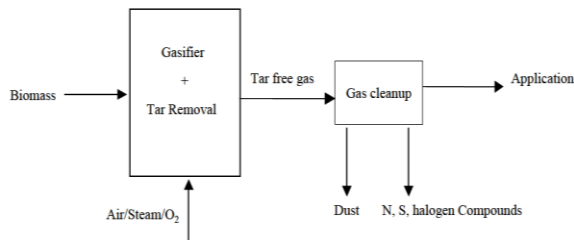


Figure 1: Primary method for tar reduction [7]

B. Secondary methods for tar removal

The secondary method includes cleaning bio-syngas by using a filter and catalyst (Fig. 2). Particulates can be cleaned by the filters, and tars in bio-syngas can be reformed by the catalysts. There are various catalysts that have been used for the tar conversion, like nickel, chromium, char, cerium, etc.

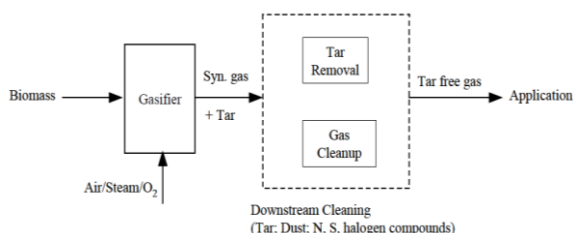


Figure 2: Secondary method for tar reduction [7]

IV. BIO-SYNGAS FILTERS (WITH SECONDARY METHOD OF TAR CLEANING)

The bio-syngas produced from waste biomass gasification has impurities like particulates, tars, etc. The dust, soot, ash, and char make up the particulate matter. The particulate matters degrade the fuel quality and also reduce the heat conversion effectiveness. Therefore, raw bio-syngas must be cleaned through suitable filtering systems. [9] studied a ceramic based catalytic filter in which a ceramic candle filter is selected for particulate removal and the Ni catalyst is impregnated on the filter candle for tar reforming (Fig. 3). It was found from the test that tar conversion efficiency can be achieved for naphthalene between 96% and 98% and for benzene between 41% and 79% at 850 °C.

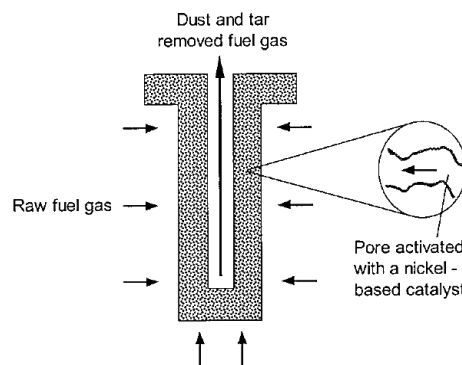


Figure 3: Schematic representation of ceramic based candle filter [9] [10] designed and developed the sand filter to remove tars and particulates from the producer gas. They have used wood shaves, coarse sand and fine sand (Fig. 4). The wood shaves were used to remove the moisture from the syngas. The coarse and fine sand were used to remove the tars and particulates from the bio-syngas. It was found from the experiment that the percentage reduction of tars and particulate matter was above 90%. [11] studied that with particle loadings of 0.1 ppm (size < 100µm) in the output stream, different ceramic based filters have been able to achieve a particulate removal efficiency of 99.99%. Table 1 shows the tar reduction efficiency of the different types of filters, with the catalytic filter having the highest tar reduction efficiency.

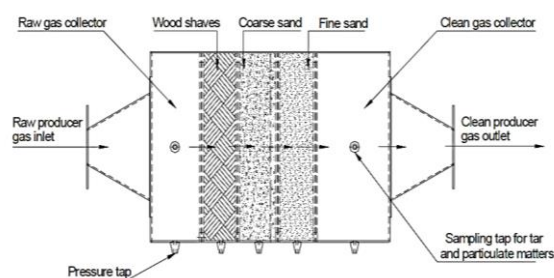


Figure 4: Schematic diagram of sand bed filter for producer gas cleaning [10]

Table 1: Different types of filters and their tar reduction efficiency

Filter Types	Tar reduction efficiency	References
Cyclone Separator	Data was not found (good enough to remove the particulates than the tars)	[4]
Rotating particle separators	30-70%	[6]
Fabric filter	0-50%	[6]
Catalytic filters	>90%	[9]

A. Catalytic filter development and performance

The researchers are focusing on development and performance study of catalytic filters those can remove product gas particles and, on the catalyst side, can reduce tars. [9] studied performance of the Nickel based catalyst impregnated on ceramic candle filter for tar removal from syngas. They also investigated the impact of temperature, gas flow rate and nickel loading on the conversion of benzene and naphthalene as shown in Figure 5. The primary variables examined were catalyst loading (0.5 and 1 wt%), reaction temperature (750–900 °C), and gas velocity (2.5–6 cm/s). It was discovered that

naphthalene can be completely converted to syngas (H_2 and CO) at 800-900°C over an activated filter candle with a loading of just 1.0 wt% nickel catalyst when typical filtration gas velocities are used. They found that at 850°C, substantial conversion activity was present.

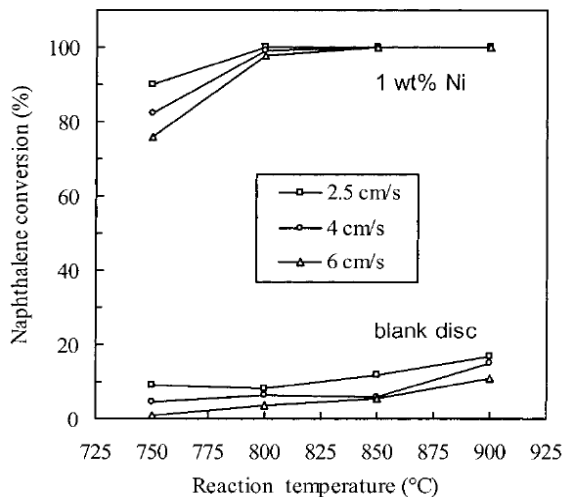


Figure 5: Effect of reaction temperature and gas velocity on naphthalene conversion over 1 wt.% nickel modified filter and blank ceramic filter [9].

[12] performed the test on Al_2O_3 based grain-sintered filter element support was first impregnated with a fine, wet-milled suspension of a $MgO-Al_2O_3$ and successively with nickel nitrate hexahydrate. To make compact gasification and hot gas cleaning unit, catalytic filter candle was inserted in the freeboard of the gasifier operating at temperature range 808-813°C. Tar yield reached the minimum value of $0.15 g/Nm^3$ and an average overall tar conversion of 93.5% was achieved. [13] performed the test on the combination of Al_2O_3 based catalytic filter and catalytic foam to improve tar reforming capacity as shown in Figure 6. A tar conversion of 99% was achieved at an operating temperature of 850 °C. An Al_2O_3 -based catalytic filter candle resulted to 98% naphthalene conversion, which was 18% greater than the conversion obtained by a SiC candle so far without incorporated catalytic ceramic foam. This demonstrates the significance of using catalytic ceramic foam in addition in order to give a technically workable solution at 850°C for effective tar reformation in hot gas cleaning of syngas obtained from biomass.

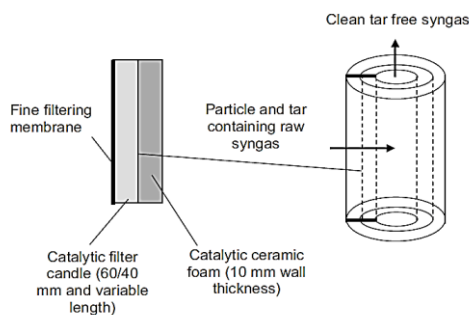


Figure 6. Structure of the catalytic filter candle with integrated catalytic ceramic foam [13]

[14] analysed performance of fixed bed catalytic filter. It was reported that as the gasification temperature increases, the tar

content in the bio-syngas decreases. Total tar concentration was $0.65 g/Nm^3$ at the catalytic filter's output in the experiment at the maximum gasification temperature (850 °C). It was also found that tar conversion reduced as the face velocity was raised from 40 to 90 m/hr as gas spent less contact time in the catalytic filter. The catalytic filter proved success in tar reduction and conversions of approximately 75% were attained in tests with various tar concentrations at the intake.

[15] conducted experiments on a ceramic candle filter for tar reformation and particle removal with filter partially and fully loaded with Ni-catalyst pellets, as shown in Fig. 7. When tests were conducted at higher temperatures and using the partially filled candle arrangement, the catalyst showed excellent results. The pressure drop in partially filled ceramic candle filter is similar to that of empty candle filter (approximate 3.5 kPa), but lower than the fully filled candle (approximate 5.5 kPa) at temperature of 800 °C and gas velocity of 2.8 cm/sec as shown in Fig. 8. Tars were decreased to $250 mg/Nm^3$, and 4 hrs testing revealed no deactivation of the Ni-catalyst.

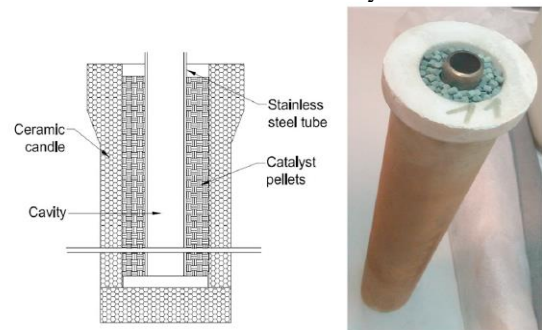


Figure 7: Ceramic candle filter filled with catalyst pellets [15].

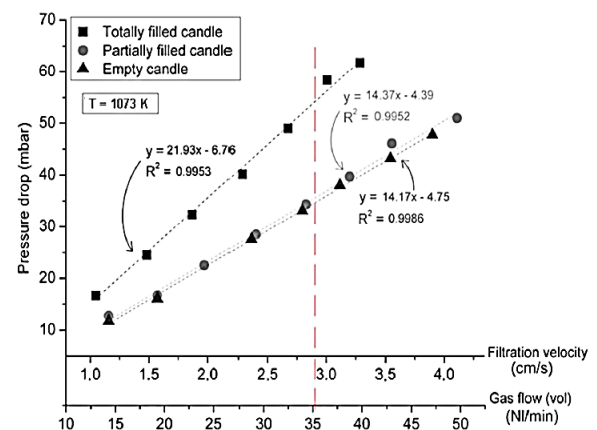


Figure 8: At 800 °C and various face filtration velocities, pressure drop through various configurations of candle filter (completely, partly filled and empty Candle) [15]

[16] studied in their paper the performances of the sol-gel Ni/ $\gamma-Al_2O_3$ catalyst under the conditions of long-term experiments and in the presence of H_2S . 10 wt. % Ni/ $\gamma-Al_2O_3$ catalyst codoped with Mn+Mo, Ca+K or Ce+K showed better resistance against deactivation than pure 10 wt. % Ni/ $\gamma-Al_2O_3$ catalyst. Straczewski et al. (2021) [8] developed a compact filter in which solid-state filtering and tar conversion can both be accomplished using catalytic filters in a single step filtration process (Fig. 9). Both the impregnation method and composition of the impregnation were studied in order to increase the tar conversion rate and long-term stability of the

catalyst at 700 °C. A ceramic fibre filter constructed of Al₂O₃ (44%) and SiO₂ (56%) that had been impregnated with a catalyst made of Ni, Fe, and Cr oxides and supported with Pt was found to be the most efficient catalyst and their effects are shown in Table 2.

Table 2: Catalysts and their effects

Catalysts	Effects
Ni	Lower in cost, most effective for tar reforming and NH ₃
Fe	Effective in NH ₃ conversion
Cr and Mn	Reduce coke formation (produced during the conversion of tar) on catalyst's surface
Ru and Pt	make the catalyst active at lower temperatures

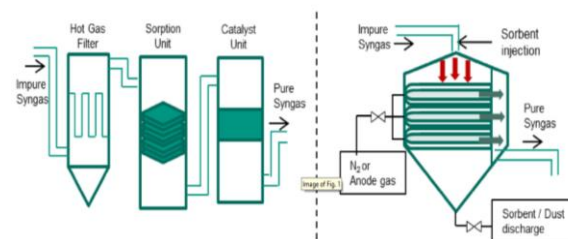


Figure 9: Gas cleaning unit in conventional biomass gasification plant (left) and a compact biomass gasification plant (right) [8].

Table 3: Performance of ceramic based filter with their catalyst used

Filter Type	Catalyst Used	Gas velocity (cm/sec)	Temp. Condition (°C)	Tar yield at filter outlet (g/Nm ³)	Conversion (%)	Reference
Al ₂ O ₃ based filter	Ni impregnation	2.5	~850	-	>90%	[9]
Al ₂ O ₃ based filter	MgO-Al ₂ O ₃	2.33	740	0.15	93.5	[12]
Al ₂ O ₃ based filter with catalytic foam	MgO-Al ₂ O ₃ foam support with NiO loading	2	850	-	99	[13]
Fixed bed catalytic ceramic filter	MgO supported Ni catalyst	1.72	850	0.65	75	[14]
Ceramic filter filled with pellets	Ni pellets	3.2	~800	0.250	-	[15]
Ceramic fiber filter of Al ₂ O ₃ -SiO ₂	Ni, Fe, Cr oxides promoted with Pt	-	790	-	98	[8]

B. Development of catalysts:

The ceramic filtering by itself is not a viable method for cleaning hot gases. It can, however, be used in conjunction with other separation methods such thermal and catalytic cracking/conversion. There are several catalysts, along with their catalytic efficiencies to remove tar from the bio-syngas that have been discussed in the review.

The development of efficient technologies for the cost-effective and optimal removal of tar is a significant area of current study. There are several advanced alternatives that promise to significantly minimise the quantity of tar. However, the technique must be economically viable, effective in removing tar, and most significantly, it must not interfere with the production of beneficial gaseous products [7]. [17] studied the comparison of the Al₂O₃ and CeO₂-ZrO₂ supported Ni catalyst. 15wt% Ni/CeO₂(75%)-ZrO₂(25%) showed higher catalytic performance and also lesser coke formation than the 15 wt% Ni/γ-Al₂O₃ and commercial Ni catalyst.

[18] presented in their paper that the deactivation of the char was due to the deposition of soot on the char's active sites. The char deactivation rate can be decreased by increasing temperature and steam concentration, which resulted in an increase in soot gasification compared to carbon deposition, resulting in a decrease in the char deactivation rate (Fig. 10).

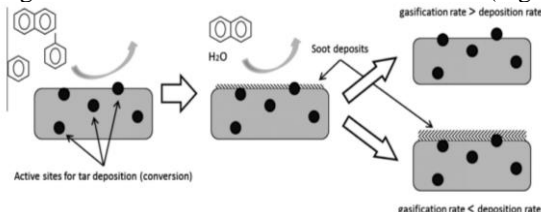


Figure 10: Representation of the mechanism for tar conversion over a carbonaceous surface. [18]

[19] studied a comparison of inactivated and activated char in their paper. The activated char showed more tar reforming

capacity than inactivated char because the activated char has more active sites with large surface area, more abundant electron-rich elements, and a more amorphous carbon structure. [20] studied the performance analysis of Ni-based catalysts with γ-Al₂O₃ and α-Al₂O₃ supports. The results showed that γ-Al₂O₃ has better H₂ yield, toluene than on the α-Al₂O₃. It showed a conversion rate of 75% at reaction conditions of 700 °C temperature.

[21] studied the tar conversion in biomass syngas by using the non-activated wood derived char. Study resulted that the tar conversion in the range of 64-73% was achieved at 875°C while test was conducted for 5 hour. Further, the tar conversion was reduced with time due to consumption of char rather than deactivation. Char is a by-product of the process (gasification or pyrolysis), it is both readily accessible and inexpensive, unless specific treatment is needed to activate it. It is also quite resistant to sulphur and chlorine toxicity and may be burned after usage. Additionally, char preferentially transforms the heavier components of the tar mixture. They showed in their paper that they used the char as catalyst in test because char is eco-friendly and lower in cost than the metal-based catalyst and also metal based catalyst can be deactivated by coking or poisoning due to the presence of the contaminants in syngas.

[22] studied the thermal breakdown of acetic acid and its reformation product utilizing catalysts including olivine, dolomite, and metal-based catalysts. The acetic acid was entirely reformed by the metal-based catalyst, and there was essentially no formation of carbonaceous deposits. When it came to the reverse water gas shift reaction and methane reforming, the metal-based catalyst had good catalytic activity, but dolomite and olivine only displayed weak catalytic activity. [23] studied Ni-based hybrid catalyst, which was prepared by Ni wet-impregnation on the peat char and sludge char mixture. The prepared catalyst performed well in terms of tar removal

and syngas performance. The catalyst was examined with different Ni/PC-SC compositions such as 5Ni/PC-SC, 10Ni/PC-SC, 15Ni/PC-SC, and 20Ni/PC-SC. The benzene removal rate can reach 91.8% at 800°C by using a 15Ni/PC-SC based catalyst. Hence, 15wt% Ni/PC-SC showed the best performance among the different compositions.

Table 4 shows the performance of the different combinations of catalysts and preparation methods. It is observed that the catalyst combination list consists of the active, promoter, and support materials. Some combinations consist solely of active and support material, and some have a bimetallic combination. But the addition of promoter to the catalyst combination

improved the conversion efficiency. Ni catalyst with promoter and support material can give more encouraging results in terms of tar conversion efficiency at comparatively low temperature of produced syngas. The biomasses are natural materials available in different geographical regions and have variability in characteristics. Therefore, the syngas produced would contain wide range of tar content and needs to be cleaned. In this regard, for sustainable development of clean fuel, the proper experimental study is required for development of filters with catalysts.

Table 4: Active catalyst with their promoters and support catalysts for the bio-syngas tar reforming reaction

Catalyst			Preparation Method	Temp. Condition (°C)	Conversion (%)	References
Active	Promoter	Support				
Ni	-	Mg-Al (Hydrotalcites)	Wetness impregnation	550	90	[24]
Ni	-	PC-SC (Peat Char-Sludge char)	Wet-Impregnation	800	91.8	[23]
Ni, Fe, Cr	Pt	Al ₂ O ₃ -SiO ₂	impregnation	790	98	[8]
Ni	CaO, MnO	Al ₂ O ₃	Impregnation	400-800	100% at 800°C	25]
Ni	-	γ-Al ₂ O ₃ & α-Al ₂ O ₃	Wetness Impregnation	700	75	[20]
Activated hardwood char	-	-	Mechanical method	850	90	[26]
Fe ₂ O ₃	-	SiO ₂ -Al ₂ O ₃	Sol-gel	500	64	[27]
Ni	MgO-CeO ₂	Al ₂ O ₃	Co-precipitation	300-800	~100% at 450°C	[28]
Ni	-	CaO-Al ₂ O ₃ (Hydrotalcite)	Co-precipitation	650	85	[29]
Ni	Fe	Al ₂ O ₃	Co-precipitation and wetness impregnation	650	90	[30]
Ni	Fe	MgO-Al ₂ O ₃	Impregnation	700	85	[31]
Ni	-	CeO ₂ -ZrO ₂	impregnation	700	87.2	[17]

V. CONCLUSIONS

Bio-syngas is one of the promising clean fuels for power generation and thermal application. This review paper represents a summary of the state-of-the-arts in syngas cleaning technology and recent development of catalysts. Filters are described, such as fabric filters, rotating particle separators, and catalytic filters, the latter of which has a higher efficiency in particulate removal and tar reforming than the others.

A good catalyst should generally have high tar conversion efficiency, be inexpensive, easy to regenerate, and environmentally friendly. Ni is a widely accepted active metal component for this reforming reaction in terms of availability and activity. It has been observed that the metallic based catalyst used for tar conversion makes the filter costly and causes rapid deactivation.

Char catalyst has higher catalytic performance than metallic catalyst and is also less harmful to the environment. The activated char has higher catalytic performance than non-activated. Both the nature of the active metal and the support material are essential for an effective catalyst. Promoters can be used in the catalyst compositions. There are various types of promoters like Fe, Cr, Mn, Pt and Ru. Cr, Mn and Ce can reduce the coke formation on catalyst and increase activity time for active catalysts. Pt and Mn can be added in the catalyst to make it active at lower temperature. The catalyst proved very

effective with a partially filled candle filter and in tests conducted at a higher temperature. To make the filter compact, both the processes of filtration and tar conversion should be combined into one step process.

From the literature survey, it is suggested that the catalyst combination of Ni, Ce and activated char can be used for further study to make it highly catalytically active, cost effective, eco-friendly, and to reduce the coke formation on the catalyst. An efficient and compact filter can be made by using the right catalyst composition and changing the design of the filter.

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