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TAR REMOVAL FROM PYROLYSIS GAS BY ANAEROBIC TREATMENT PROCESS

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Syngas, Gasification,
Tar,
Biological removal,
Treatment.

Abstract

One of the most significant current discussions in today is the Energy conversion Technologies and clean energy suppliers. The past decade has been viewed the rapid development of energy conversion technologies. During this development, many energy production technologies have been found and researched. One of them is biomass thermal conversion systems, which are examined under three titles as pyrolysis, gasification and combustion. However, the major problem of thermal conversion systems is tar amount and composition in the product gas. The tar is a side product and causes problems in the systems emerging as the by-product of thermal conversion systems such as gasification and pyrolysis. Tar is condensed below dew point temperature and accumulated in the system and causes heat losses, corrosion, soot formation, catalytic poisoning, and congestion in pipes and ducts. In this study, a new tar removal system has been designed with the hybrid operation of biogas and pyrolysis systems. The pyrolysis reactor and the biogas reactor are operated in connection with each other in the system. The amount of tar was determined via gravimetric analysis method as 0.159, 0.194 and 0.165 g/L respectively in the pyrolysis gas of 10, 20 and 30 L. The main purpose of this study is to examine the effects of biological treatment method, which is a new method in tar treatment, and also to add a new hybrid treatment method to the literature. In this system, the pyrolysis gas, which has tar content, was passed through the biogas reactor and the yield was calculated as 55.08 %, 56.01 % and 56.09 %. The highest yield was calculated as 56.09 %.

PİROLİZ GAZINDAN ANAEROBİK FERMANTASYON YÖNTEMİ İLE TAR ARITIMI

Anahtar Kelimeler
Sentez gazı,
Gazlaştırma,
Tar,
Biyolojik arıtım,
Arıtma teknolojileri

Öz

Bugünün en önemli tartışmalarından biri Enerji dönüşüm teknolojileri ve temiz enerjidir. Son on yılda, enerji dönüşüm teknolojilerinin hızlı gelişimi gözlenmektedir. Bu gelişme sırasında birçok enerji üretim teknolojisi bulunmuş ve araştırılmıştır. Bunlardan biri, piroliz ve gazlaştırma gibi biyokütle termal dönüşümdür. Bununla birlikte, bu tür dönüşüm sistemleri ile ilgili önemli bir sorun, ürün gazı yan ürünü olan katran miktarı ve konsantrasyonudur. Katran, gazlaştırma ve piroliz gibi termal dönüşüm sistemlerinin yan ürünü olarak ortaya çıkan sistemlerde sorunlara neden olan istenmeyen bir yan üründür. Katran sistemde, çiğleşme noktasının altındaki sıcaklıklarda yoğuşarak reaktör, boru ekipmanları ve diğer sistem ekipmanları üzerinde birikerek ısı kayıplarına, korozyona, kurum oluşumuna, katalitik zehirlenmeye ve boru ve kanallarda tıkanıklığa neden olur. Bu çalışmada, biyogaz ve piroliz sistemlerinin kombine çalışması ile yeni bir katran parçalanması sistemi tasarlanmıştır. Piroliz reaktörü ve biyogaz reaktörü sistemde birbiriyle bağlantılı olarak çalıştırılır. Katran miktarı, 10, 20 ve 30 L'lik piroliz gazında sırasıyla 0.159, 0.194 ve 0.165 g / L olarak gravimetrik analiz yöntemi ile belirlenmiştir. Bu çalışmanın temel amacı, literatüre yeni bir katran parçalanmasını sağlayan biyolojik arıtım yönteminin kazandırılmasıdır. Bu sistemde katran yan ürünü ve piroliz gazı biyogaz reaktöründen geçirilerek verim % 55.08, % 56.01 ve % 56.09 olarak hesaplanmıştır. Burada en yüksek verim % 56.09 olarak tespit edilmiştir.

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1. Introduction

The energy demand has been doubled in developed countries with increasing population and electricity consumption. Today, the most important problems of the energy are narrow resources of fossil fuels, the energy security problem, and the negative effect of gas emissions on global warming. Therefore, use of renewable sources increase day by day. One of renewable energy source is biomass and different conversion technologies have been used for it. One of them is thermal conversion technologies. The biomass gasification and pyrolysis systems are called thermal conversion systems. They are clean and highly efficient systems alternative to fossil fuels (Anis&Zainal, 2011). The product gas which generated during thermochemical conversion technologies is used in internal combustion engines, gas turbines, fuel cells, and power and heat systems. The product gas composed of H_2, CO, CH_4, CO_2, nitrogen, stream and heavy hydrocarbons which is known as tar. The tar is the common pollutant in the product gas and is regarded as the biggest obstacle to the wide and commercial application of biomass thermal conversion systems (Asadullah, 2014). The equipment pollution has been made flow difficult in the systems, tar has been caused several problems such as blockage, contamination, corrosion, and abrasion. The amount of tar in the gases produced during biomass thermal conversion range from 0.5 to 150 g/Nm³ (Shen, 2015). The tar impurities are the complex organic components which include hydrocarbons varying from light components like benzene to polyaromatic hydrocarbons. Formation of tar depends on the type of process and working conditions. Another definition of tar is components with boiling point above 150°C (Ahmed, Salmiaton, Choong & Azlina, 2015). In gasification systems, parameters like reactor type and geometry, amount and type of oxidant, type of fibers, temperature and pressure directly affect the amount of tar (Poethanom et al., 2012). Temperature is one of the most significant parameters for tar composition on pyrolysis systems. The formation of tar starts with the transformation of biomass into primary tar products below 650°C and more complex polyaromatic hydrocarbons observe at the higher temperatures. There are primary, secondary, and tertiary stages of tar formation with increasing temperature. Primary pyrolysis regime is the formation of oxygenates at between 400-700°C which are primary gas products (Poethanom et al., 2012). Secondary hydrocarbons have been called phenols and olefins emerge at between 700-850°C. Amount of tar varies depend on the reactor type, sort of raw material and working conditions. The different tar tolerance values have been shown depending on the application areas of the pyrolysis gas at Table 1. The tar tolerance values are 50 mg/Nm³, 50 mg/Nm³ and 8 mg/Nm³ for internal combustion engines, methanol synthesis and gas turbines, respectively (Milne & Abatzoglou, 1998).

Table 1

Synthesis gas application areas and tar tolerances (Suzuki and Li, 2009).

Application Areas	Tolerance values(mg/Nm³)
Burner	-
Combustion engine	10-50
Turbines	8
Methanol Synthesis	<0,01
Fuel cell	<1

Tar impurities has to be reduced to acceptable limits to prevent any problems in usage areas. Therefore, many tar treatment technologies have been researched and developed in literature. In general, waste treatment systems have been classified as thermal cracking, catalytic cracking, mechanical treatment, and physical treatment technologies (Paethanom, Nakahara, Kobayashi, Prawisudha & Yoshikawa, 2012).

Thermal cracking techniques are performed at high temperatures such as 1200-1300°C. Thermal treatment method is quite effective, but it is complex and costly. Another method is catalytic cracking takes place at high temperatures with catalysis. Ni-based catalysis is used commonly in this method. Tar removal efficiency of catalytic cracking method is 97 %. But it has some disadvantages such as used catalysis amount and catalysis poisoning (Paethanom et al., 2012). Physical tar treatment methods are divided into two different parts: wet and dry methods. The dry systems are fabric filter, ceramic filter, cycling and sand bed filters. The dry systems are not suitable for tar removal because of tar accumulation on filters. The wet systems are found to be effective on removing tar. These methods have been preferred due to easily adaptation into the gasification systems, economic advantages and high tar yield (García, Pizarro, Lavín, & Bueno, 2017). The wet systems are generally compose of spray towers, wet cyclones, and wet electrostatic precipitators. These systems are easy to set up and use, but their efficiency levels are low. For the selection of the effective gas cleaning method, the nature and type of tar pollutant should be identified firstly. The second step of cleaning system is gasifier design for reduce the tar amount in the system. In the gasifier design, generally downdraft gasification prefers for low tar content. Another step is determining the appropriate heat, sustentation type and oxygen amount, namely optimum operating conditions.

Gasification systems include different reaction conditions (Mayerhofer, Mitsakis, Meng, Jong, Spliethoff & Gaderer, 2012). In the reverse flowing fixed bed gasification, high amount of tar (100-150 g/Nm^3) is produced at low temperatures during pyrolysis stage. On the other hand, co-current and fluidized bed gasification produce low level (<20 g/Nm^3) tar. Operation conditions of gasification play an important role for tar formation and reduction. The most critical parameters are heat, excess air, steam/biomass proportion and waiting time. Tar reduction more than 40% has been occured at 700-900°C. Ideal excess air range is determined as 0.2-0.3 for appropriate tar reduction and gasification (Narváez, Orío, Aznar & Corella, 1996). The success of tar treatment system is not only depend on tar amount but also depends on its characteristics and composition. The 5th, 4th and 2nd classes of tar concentrate on systems, obstruct the motors and turbines. Especially, these classes of tar are taken in the account during processes development. Being one of the most important problems of biomass usage and producing from thermal processes, tar gives a broad scope of damages to boilers, transfer lines and internal combustion engines due to condensing at low levels. Because of these reasons many researches are conducted on determining ingredients of condensable hydrocarbons named as tar emerging during gasification process and on developing tar treatment methods (Suzuki & Li, 2009). In this research, combination of thermal and biological systems which is the new method in the literature are used for the removal of tar from pyrolysis gas. Cattle fertilizer has been used for biological tar treatment as absorbent. The most significant advantages of biological treatment systems are economic, simple, and high efficiency

2. Material and Method

In this paper, the experiments have been examined under three stages. Research and publication ethics have been followed in this study. Firstly, appropriate feeding material for pyrolysis has been determined as and use as weight 70 and 100 g respectively for pre-pyrolysis experiments. The characterization of sawdust has been measured with raw material analysis. The result of analysis, the particle size of the sawdust, the moisture content and the heat value have been determined as 2 mm, 6.7 % 17632 kJ/kg , respectively. The results of raw material characterization have been explained in the part 2.1. with all details. Secondly, the quidline method has been used for gravimetric analysis. The amount of tar has been measured in syngas with quidline method (Milne & Abatzoglou, 1998). At last stage of experiments, remaining waste of cattle fertilizer coming from anaerobic fermentation has been used as tar absorber. The pyrolysis reactor and gas storage tank have been shown in from Fig.1. The temperature of the reactor has been measured by temperature indicator during experiments. The reactor dimensions have been chosen as 25 cm in length and 60.57 mm in diameter. Also, syngas has been stored at atmospheric pressure in the gas storage tank shown in Figure 1b. The thermometer has been used to the control of reactor temperature. Impermeability of all joints have been provided by oring and heat resistant paste. The sawdust that has been weighted as 70-100 g and placed and heated in the reactor at designed temperature and the pyrolysis process has been started by linking 250W of 310 stainless steel resistors within reactors to power supply. The reactor inlet has been sealed hermetically; outlet has been linked to gasification by appropriate joints. The experiments have been continued 60 minutes until finished product gas that exit from reactor. In the first step of experiments, gas has been produced in the pyrolysis reactor send to gas collection unit. The amount of solid product has been determined by weighting the remaining solid product in the reactor.

Figure 1. Pyrolysis Experiment Setting Flow Scheme
a) Pyrolysis reactor b) gas storage tank

The pyrolysis process has been operated at 50°C/min heating speed and the system has been kept stable at 500-600°C. The product gas has been passed to washing bottles as shown in **Figure 2**. The acetone and isopropyl have been used as solvent for washing line. The before the tar treatment experiments with 6 washing bottles, the line has been cleaned with solvent at an hour at 50°C. The glass beads have been used as heat mixer in the bottles. The 75 mL dissolvent has been put at first 5 bottles, the last bottle was left empty as humectant. The acetone and isopropyl have been used as dissolvent in the bottles because of their highly absorbent nature for tar pollutants. The water bath in which first 3 of bottles have been placed and kept at 35°C, in which last 3 of bottles have been placed and kept at 0-5°C. The gas, which reaches to 300-350°C temperature at outlet of the reactor has been passed through 6 gas washing bottles and filled with dissolvent of tar. The gas has been passed through bottles for an hour so that tar can be absorbed within the dissolvent. The absorption amounts of tar within washing bottles has been observed with color change and dissolvent materials as seen in the given experiment setting at **Figure 2**. The distribution of tar concentration has been decreased from first to last bottle. The absorption of tar components within dissolvent has been started at 350°C which is dew point of tar (Milne & Abatzoglou, 1998).

According to experiment analysis, the tar absorption amounts of acetone and isopropyl has been compared.

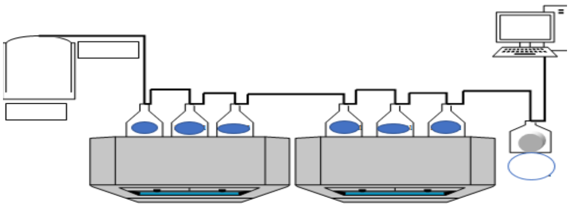

Figure 2. Determining Tar Amounts by Gas Washing Bottles

In this study, the pyrolysis process and anaerobic fermentation has been integrated. The cattle fertilizer has been used as raw material for biogas process and fermented waste has been obtained from 25 m^3 biogas facility established by Energy Technology group of Solar Energy Institute at İzmir Torbalı. The gas product with high concentration of tar which coming out from pyrolysis reactor in experiment has been combined with anaerobic fermentation process without using chemical, mechanical, physical treatment methods, and tryouts for biological treatment of tar has been performed. The 10 amber bottles with 1L volume has been used as fermentation reactor and within reactor fermented waste which acquired as result of biogas production by using cattle fertilizer. In the normal conditions, the bacteria population in biogas system has been inhibited and affected environmental conditions. However, the cattle fertilizer has been used anaerobic fermentation biogas has been occurred and after the gas exit process has been completed. The syngas has been passed to fermented cattle fertilizer and tar absorbed on fermented cattle fertilizer. The main reason for using cattle manure in this study is that it is suitable for biogas production and includes a population of bacteria that can adapt to mesophilic and thermophilic conditions. In this way, adaptation has been achieved by only slowing the process without the need to cooling the syngas. So that, bacteria population has been continued to produce gas with the adaptation of bacteria in this system. Cattle manure completed the fermentation process to prevent the bacteria from dying and adapting to the system. The synthesis gas which has been emerged by pyrolysis has been passed from bottles at 10, 20 and 30 L volumes respectively, as given in **Figure 3**. The experiments have been performed as 3 parallels. As a result of experiment, the tar components have been treated with integrated biogas and syngas system. To determine the amount of the gas emerging in this setting which consists of the integration of pyrolysis and anaerobic fermentation, anaerobic reactors are put to a warm room at 35^{0}C after gas transfer.

The exit gas of anaerobic systems has been measured and the tar amounts of gas have been calculated with guideline method which used in the first part of the experiment. To strengthen results of the gravimetric analysis, wavelength analyses have been performed.

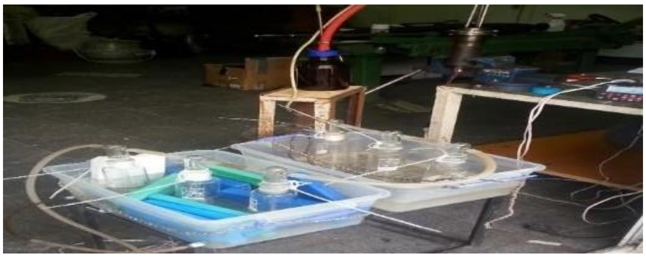

Figure 3. Syngas Tar Treatment Process

2.1 Biomass Short Analyses

All analyses have been performed as 3 parallel experiments and average of acquired data has been calculated.

2.1.1 Determination of Moisture

The determination of moisture of sawdust has been used in experiments. The fermented waste and tar components have been performed according to ASTM D 2016-74 standards. To the determination of moisture, the samples have been dried within drying oven which kept at 103±2 °C. During determination process 2.00±0.05 g material has been weighted, then the sample has been dried till reaching fixed weighting after half time weightings, and percentage moisture of intake has calculated by equation 1 (Basu, 2010).

$$\%Moisture = \frac{\mathrm{m0} - \mathrm{m1}}{m1} * 100 \qquad (1)$$

m0=Starting experiment sample, g

m1=Dried experiment sample, g

2.1.2 Determination of Volatile Solids

The experiments have been performed by ASTM E 897-82 standards. Approximately 2 g of biomass sample has been weighted by 0,1 mg sensitiveness. The crucible has been covered by its bracelet and put into the oven at 900±20°C. It has been paid attention for biomass sample not to burn. It has been waited in the crucible for 7 minutes, put out and cooled in the desiccator, then weighed. The number of volatile solids in biomass sample has been determined by equation 2 (Basu, 2010).

$$VS(\%) = (\frac{[g1 - g2]}{g2} - M) * 100 \qquad (2)$$

g1: weight of used biomass sample (g)

g2: weight of biomass after heating (g)

M: moisture percentage of the used biomass sample

2.1.3 Determination of Ash Content

The experiments have been performed by ASTM D 1102-84 standards. Firstly, crucible which has been used for determination of ash content and its bracelet has been burned for 2 hours in ash furnace at 550^{0}C and brought to fixed weighing. Then it has been placed in the desiccator and left cooling down. Its empty weight (tare) has been measured and noted. The sample as 2 g has been weighed and then burned for 2 hours within ash furnace. After the burning process, it has been placed in the desiccator and left cooling down, then weighed and noted. The calculation of ash percentage has been determined from equation 3 (Basu, 2010).

$$\text{Ash\%} = \frac{M1 - M2}{\text{M3}} * 100 \qquad (3)$$

M1: Last weighing (g)

M2: Tare (g)

M3: Weighing of the sample (g)

2.1.4 Determination of Fixed Carbon

After determining volatile solids, fixed carbon has been determined according to following equation:

$$Fixed\ Carbon\% = 100 - (Volatile\ Solid\% + Moisture\% + Ash\%) \qquad (4)$$

2.1.5 Elemental Analysis of Raw Material

The elemental analysis of feeding sawdust has been made by using Truspec CHN-S device which is calibrated by ASTM D-5373 and ASTM D-4239 standards. The percentages of oxygen have been calculated. For this analysis, raw material has been placed in a special capsule and weighed sensitively. During analysis, the capsule is automatically transferred to burning reactor, and the oxygen has been burned at 1700-1800^{0}C. The elemental peaks formed according to proportions of elements and C, H, N and O percentages of sawdust and fermented waste has been determined (Basu, 2010).

2.1.6 Determination of Calorific Value of Raw Material

The calorific value has been determined by two way. The higher calorific value was defined as the emerged heat energy when product water of combustion reaction is in the liquid phase. The lower calorific value was defined as the emerged heat energy when product water of combustion reaction is in the vapor phase. The Lower calorific value of lignocellulosic biomass is between 15-19 MJ/kg. The higher calorific value has been determined with adiabatic bomb calorimeter as 25^{0}C by enthalpy differences of product and intake. The higher calorific values of materials have been calculated on the bomb calorimeter which is calibrated by ASTM D-240 and ASTM D-5865 standards, and the lower calorific values of materials have been calculated by using hydrogen percentages on transformation formulas. Also, the high calorific values of raw biomass and pyrolysis products have been calculated by following equations of 5, 6 and 7 and then compared (Dalia, Mamdouh, Gadalla, Abdelaziz, Hulteberg & Ashour , 2017).

$$HCV\ (HHV) = 354{,}68\, C + 1376{,}29\, H + 71{,}26 - 15{,}92\, Ash - 124{,}69\, (O + N)\ KJ/Kg \qquad (5)$$

$$HCV\ (HHV) = 33{,}83\, C + 144{,}3\, (H - O/8) \qquad (6)$$

$$HCV\ (HHV) = 33{,}5\, C + 142{,}3\, H - 15{,}40 - 0{,}145\, N \qquad (7)$$

2.1.7 Fiber Analysis Method

The sawdust consists of 3 natural polymers: cellulose, lignin and hemicellulose. In woody plants there is 10-30% lignin, 30-70% cellulose and 20-30% hemicellulose (Patuzzi et al., 2013). The Ankom fiber analysis device has been used to determine cellulose, hemicellulose and lignin ratios of sawdust and pyrolysis product. Firstly, the samples have been put into reaction with neutral detergent for 75 minutes at 100^{0}C, then dried for 2 hours at 104°C, then 0,5 g of the sample has been mixed with neutral detergent solid solution within analysis device, and lastly 4 mL amylase enzyme and 20 g sodium sulphide is added to mixture. The samples have been washed with hot water and bring out from device 75 minutes later, then waited in acetone. Then samples have been dried and weighed at 104^0C. Acid detergent solid has been prepared as solution in 2 L 0,255 N sulphuric acids. The dry material has been weighed as 0,5 g at filter bags and reaction has been performed for 60 minutes at 100 °C. Then products have been weighed again and kept in 72 % sulphuric acid solution for 3 hours. Then, dried for 2 hours at 104°C. During neutral detergent analysis cellular components have been removed and only the hemicellulose, cellulose and lignin left at filters. These materials have not been dissolved at neutral ph. All the hemicellulose has been dissolved in the acid detergent analysis and cellulose has been dissolved within 72 % sulphuric acid solution. Lignin, cellulose, and hemicellulose ratios of sawdust have been determined by help of this method (Basu, 2010).

2.1.8 Spectrometer Analysis Lambert-Beer's Law

Lambert-Beer's law has been used to determine tar distribution in 250 mL six gas washing bottles. Extinction coefficients of tar components like naphthalene, phenol, biphenyl, and acenaphtalene have been found out from literature, then their concentrations have been calculated by Lambert-Beer's equation. Maximum wavelength has been determined as 285 nm and sample path length has been taken as 1 cm. Units of the equation have been decided as follows: mol/L for concentration, cm for I, and L mol^{-1} cm^{-1} for extinction coefficients (Dalia et al., 2017).

$$A = \epsilon * l * c \qquad (8)$$

2.1.9 Gravimetric Analysis of Tar Components

The hydrocarbons within product gas have been measured for tar analysis according to CEN/TS 15439 standards after concentrating. For this method isopropyl alcohol and acetone has been used as dissolvent. In this method, gas coming out from gasification reactor has been transferred through six gas washing bottles which contain dissolvent. First three bottles have been kept in -5°C water bath, last three bottles kept in 20^0C water bath. So, gas has been exposed to cold and warm effect respectively, tar within gas has been concentrated and accumulated within bottles. Then, gravimetric tar content has been determined as the following below equation, and components and their proportions within tar have been determined by tar sample which is sent to GC-MS. For gravimetric analysis, all dissolvent and tar within bottles have been gathered in 500mL balloon container and then tar has been separated from its dissolvent at rotary evaporator at 50°C, 360 mbar, then tar and dissolvent are gathered in 2 different containers. Tar mass has been determined as weighing tar container balloon. Gravimetric tar amount has been determined by dividing founded tar to washed gas amount. Tar which is separated from its dissolvent has been waited at 4°C for gravimetric analysis (Basu, 2010).

$$\mathrm{C} = \mathrm{m} * \frac{Vt(Tg + 273)}{273 * VsVg} \qquad (9)$$

m = Amount of tar (g)

Vt = Volume of washed gas (m^3)

Tg = Temperature of gas (◦C)

Vs = Volume of tar solution (mL)

Vt = Total sample volume (mL)

3. Results

The sawdust which is used as feeding material has been consisted of C, H, N and O 44.5 %, 5.58 % , 0.32 % and 47.9 % respectively according to elemental analysis results. The calorific value of sawdust has been calculated as 17632 kJ/kg. Calorific value has been calculated three different ways: Dulong equation, stock equation and experimentally due to ASTM D 240 standards. Amounts of sawdust, which is used in experiments, and fermented volatile solid waste have been found as 88.42% and 61.95% respectively, and their humidity contents have been found as 5.59% and 7.5 % respectively. To use biomass in pyrolysis process, amount of volatile material should be above 65% and amount of humidity should be less than 10%. According to this information characteristics of sawdust has been found as suitable raw material for pyrolysis. Within 40 minutes 28 L product has been acquired from sawdust. The feeding has been made on discontinuous system and all feeding materials placed to reactor as 70 g. The tar impurities in the syngas that give great damage to systems have been called as PAHs. The PAHs have been emerged at 800-900◦C. Because of that reason pyrolysis processes has been kept at 800-900^0C during tar treatment stage of this study. The effect of heat on pyrolysis process has been clarified by these studies. When heat increased, gas product is also increased, and liquid and solid products have been decreased. At 500-700° C, 12 L gas has been produced with 70 g sawdust within 1 hour, while 35 L produced at $800\text{-}900^0$C. Distribution of products have been acquired by pyrolysis process is given at Table 2.

Table 2

Distribution of products acquired by the pyrolysis process

Temp. (ºC)	Solid (%)	Liquid (%)	Gas (%)	Total conv (%)
850	39.39	4.98	59	60.6
950	29.67	5.19	65	70.3

The yield distribution of solid, liquid and gas products in pyrolysis process at different temperatures have been shown in Table 2. The high temperature of pyrolysis has been decreased yield of solid products and increased gas and liquid products. Total conversion of carbon has been increased with increase efficiency of liquid and gas. Total conversion of carbon has been calculated 60.6 % at 850 ^{0}C and 70.3 % at 950 °C. The gas product amount in pyrolysis experiments ranges within 20-30 % of feeding materials. This value increases when heat increase. Experiments have been performed after raw material selection as sawdust. The all parameter that affect to experiments, such as heat values, acquired gas products and amounts of feeding materials have been given in Table 3. Consequently, it has been decided to perform pyrolysis with sawdust at 500-600°C for 1 hour. These results have been used at experiments performed with gas washing bottles.

Table 3

Parameters of pyrolysis experiments

	LHV (kcal/m3)	Gas (L)	Feed (g)	Energy density (%)
Exp-1	3372	32	69	38.12
Exp-2	2418	24	72	19.89
Exp-3	1816	4	65	2.75

In the 2nd stage of the study, the pyrolysis gas has been passed through gas washing bottles. By transferring the synthesis gas which produced by pyrolysis process through gas washing series tar pollutants have been retained within dissolvent, and then gravimetric analyses of these tar pollutants have been performed.

The gravimetric tar analysis results have been shown in Table 4. According to this result, the gas washing bottles filled with acetone has been found more effective than filled with isopropyl. The retention capacity of tar from 70 g sawdust pyrolysis has been measured as 3.5 g and 5.27 g in isopropyl and acetone respectively during 1 hour process time.

Table 4

Gravimetric tar analysis results of gas washing bottles

Time	Solvent	Gas (L)	Impinger (º C)	Bath-1 (º C)	Bath-2 (º C)	Tar (g)
1 h	Acetone	24	350-400	25-35	0-5	4.95
1 h	Acetone	28	350-400	25-35	0-5	5.82
1 h	Acetone	20	350-400	25-35	0-5	4.04

The tar components which acquired after pyrolysis experiment and retained by dissolvent have been kept at 4^{0}C for gravimetric analysis after separated by rotary evaporator. The desired measurements for determining gravimetric tar concentrations have been performed by guideline method and results are given at Table 5.

Table 5

Required data for gravimetric tar analyses of tar which retained by acetone

	1. Exp	2. Exp	3.Exp
Sample after evaporation (g)	4.04	6.82	4.95
Tar solution in sample (mL)	328	319	318
Total tar volume (mL)	15	5	11
Gas volume of sample (m^3)	0.020	0.020	0.024
Temperature of gas ˚ C	50	50	50

Generally, the concentration of tar which emerged after pyrolysis differs between 500 mg/m^3 to 300 mg/m^3 due to features of the pyrolysis process. The average gravimetric concentration of tar which has been acquired during studies from 70 g feeding material by acetone has been determined as 0.172 g/L. In order to determine distortions and concentrations of tar pollutants components, wavelength analyses performed at spectrometer according to Lambert-Beer's law based on light transmittance after gravimetric analyses. The concentration values of hydrocarbons within bottles have been calculated according to Lambert-Beer's law according to extinction coefficients at 285 nm as indicated in Table 6 which founded from literature (Patuzzi, Roveda, Mimmo, Karl & Baratieri, 2013).

Table 6

Components according to extinction coefficients (Patuzzi et al., 2013)

Component	€ (L/mol. cm)
Fenol	2.64
Indane	1.90
Naftalin	2.38
Acenaphthen	2.64
Bipheny	3.08
Acenaphthylen	3.30
Anthracen	0
Pyrene	3.22

Absorption values of tar which retained within gas washing bottles have been determined from 1st to 5th bottle respectively 0.3514, 0.1545, 0.1195, 0.0976 and 0.0205 at 285 nm wavelength the spectrometer. The concentration distributions of components in gas washing bottles due to extinction coefficients have been determined from 1st to 5th bottles. According to calculations, the concentration values of phenol, indene, naphthalene, acenaphthylene, biphenyl, acenaphthene and pyrene components of tar have been determined as 0.1331, 0.1849, 0.1476, 0.1331, 0.114, 0.106 and 0.109 mol/L respectively. Similarly, distributions of tar components in the 2nd bottle are given which found after analyses performed at 285 nm wavelength. The concentration values of phenol, indene, naphthalene, acenaphthylene, biphenyl, acenaphthene and pyrene components of tar have been shown in Figure 4 and 5 with all details.

The tar retention amount of fermented waste has been determined by increasing amount of transferred gas. To gravimetrically calculate retained tar, fermented waste has been jointed at the end of the system. At this stage of experiment acetone, which observed at gas washing serial that has more retention capacity compared to isopropyl, has been used. Respectively 10, 20 and 30 L gas has been transferred through 3 bottles which filled with fermented waste and then waited at 350C warm room. One amber bottle which gas has not been transfer through is put to warm room as standard and recorded 12 days gas outcome. The amounts have been acquired by transferring approximately 10 L gas through fermented waste are given in Table 7.

Table 7

10 L gas treatment tryouts with anaerobically fermented vaccine

Exp.	Sawdust (g)	Before pyrolysis fertilizer (g)	Time (dk)	After pyrolysis fertilizer (g)	Cleaned gas (L)
F-1-1	25.90	1321.28	60	1324.86	10
F-1-2	25.69	1321.69	60	1324.45	10
F-1-3	30.61	1306.10	60	1310.06	10

Amounts of product which acquired by transferring approximately 20 L gas through fermented waste have been given in Table 8. The tar retention amounts for 10, 20 and 30 L gases have been determined by gravimetrical analysis results of tar after experiments.

Table 8

20 L gas treatment tryouts with anaerobically fermented vaccine

Exp.	Saw dust (g)	Before fertilizer pyrolysis (g)	Time (dk)	After Fertilizer pyrolysis (g)	Cleaned gas (L)
F-2-1	54.51	1303.60	60	1307.05	20
F-2-2	57.38	1322.95	60	1326.23	20
F-2-3	53.42	1353.79	60	1357.60	20

Amounts of product which acquired by transferring approximately 30 L gas through fermented waste have been given in Table 9. According to gravimetric analysis results, the gas volume has not been effective parameter for tar retention substantially. The effect of gas volume on tar retention has been shown in Table 10. However, gravimetric measurement has been decreased with increasing gas volume and reach the optimum quantity. To calculation tar conversion yield in biological treatment method. The desired data before and after anaerobic treatment has been shown in Table 10.

Table 9

30 L gas treatment tryouts with anaerobically fermented vaccine

Exp.	Sawdust (g)	Fertilizer before pyrolysis (g)	Time (dk)	Fertilizer after pyrolysis (g)	Cleaned gas (L)
F-3-1	71.63	1325.27	60	1328.73	30
F-3-2	75.03	1313.75	60	1317.08	30
F-3-3	75.38	1342.96	60	1345.83	30

These data have been found from pyrolysis process, gravimetric tar measurement and syngas passing from fertilizer cattle.

Table 10

Gravimetric tar amounts (g/m3)

Exp.	Tar (g)	Gas Volume (L)	Gravimetric result (g/L)	Gravimetric result (g/m3)
F-3	2.27	30	0.075	75.7
F-2	1.78	20	0.089	89
F-1	1.59	10	0.159	159

The yield of this fermented waste treatment has been calculated as 56.49%. However, assuming that there can be external agents which may increase the weight of fermented waste other than tar, the accuracy of analysis has been tested by gravimetric analysis measurement of bottles which filled with acetone. In addition to gravimetric analyses of tar pollutants, distortions and concentrations of components have been founded with the help of wavelength feature. The absorbance values of tar components for 30 L gas have been measured as 0.3068, 0.2741, 0.2449, 0.1701 and 0.1249 from 1st to 5th bottle respectively at 285 nm wavelength which defined at spectrometer according to Lambert-Beer's law. By wavelength analyses the value of indene component which founded as the maximum in the ingredient of tar has been determined as 0.18 mol/L at the 1st bottle and as 0.0108 mol/l at the 5th bottle. By wavelength analyses which performed after tar retention by fermented waste, amount of indene component has been measured as 0.16 mol/L at the 1st bottle and as 0.065 mol/L at the 5th bottle. All these results have been compared with gravimetric analysis method. Consequently, parallel data has been acquired. According to experimental results, tar component values have been decreased after anaerobic treatment, component distribution values of bottles are show that Figure 4 and Figure 5. This research has been investigated about new biological tar treatment method. In this method, hybrid system has been used in the experiments. The sawdust has been used as feed material because it is eco-friendly and sustainable structure.

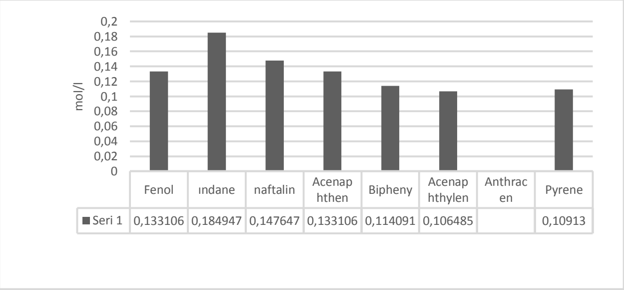

Figure 4. Component Distribution of Tar Impurities After Gasification in the 1st Bottles

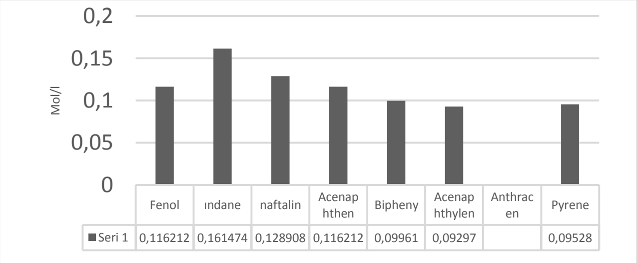

Figure 5. Component Distribution of Tar Impurities After Anaerobic Treatment in the 1st Bottles

Also, in the biological treatment part cattle fertilizer has been used as retention tar material. In literature, there are different tar treatment methods and it has been found limited resource for biological tar treatment. The cattle fertilizer has high methane content. The cattle fertilizer has been used in these experiments due to the properties of bacteria. These bacteria's adapt to mesophilic and thermophilic conditions. So, it has high resistance to temperature change interval in the system. In this study, bacteria has been adapted by passing the pyrolysis gas gradually through fermented fertilizer while the anaerobic fermentation continued. At this point, it is necessary to avoid sudden changes. To determined characterization of biomass raw material some analyses have been made such as humidity, elemental analysis, ash, GC, bomb calorimeter. According to these values' usage of sawdust as biomass material is thought as appropriate. The increase of humidity of biomass would cause some negative circumstances such as reducing energy value of biomass as an energy resource, increasing water ingredient of liquid product and oxygen ingredient of biomass being redundant. Similarly, being redundant of ash ingredient would cause biomass sample to create corrosive impact within reactor and efficiency of solid product to stay high. According to elemental analysis results H/C ratio is determines as 0.13 and being between 1-2 of this value means it may be appropriate to use related biomass as liquid fuel. Being under 1 of H/C value means biomass can be used as solid fuel, being about 4 means it can be used as gas fuel. Being 1.07 of O/C ratio means oxygen rate of biomass is higher than its carbon rate. Having high oxygen rate reduces energy content. Efficiencies of products are reducing due to resources with high oxygen ingredient. Increasing pyrolysis value up to 800^{0}C increased gas product amount at pyrolysis experiment while reducing solid product efficiency. According to results which are determined by spectrometer, maximum PAH of tar ingredient has been determined as indene, naphthalene, acenaphthene, and biphenyl, respectively. Biphenyls are also known as the most harmful PAH to the environment. After this experiment, tar retention with fermented waste has been performed which is 3rd stage of experiment. By these analyses, values of fermented waste have been determined as 7.5 % solid material, 7.35 pH, 92.5 % humidity and 61.95 % volatile solids. PH range of normally performed fermentation should be 6.6-7.6, appropriate volatile solid range for cattle waste should be 75-85 %. Reaching close results shows fermented waste is suitable for experiments. During fermented waste experiments in order to determine retention amount of tar which transferred through system, gas washing serial which filled with acetone dissolvent has been added at the end of the experiment setting and efficiency of tar which retained in fermented waste has been calculated. A net relationship has not been established between transferred gas amount and retained tar amounts. Considering tar amount retained in acetone dissolvent, efficiency of retained tar for 30 L gas transfer through fermented waste is determined as 56.09%. At the same time, amounts of tar which accumulated within bottles after tar treatment with fermented waste and after gas washing have been calculated according to Lambert-Beer's law and decrease in tar amounts from 1st to 6th bottles have been observed. Decrease in absorbance values from 1st to 5th bottles has been observed according to spectrometer results. After 10, 20 and 30 L gas transfers, fermented waste has been kept at 350C warm room for 12 days to observe the gas outcome. Reactions of fermented bacteria to tar pollutants which emerged from polyaromatic hydrocarbon mixture has been observed. During this process, no gas outcome has been observed and great changes in pH values and alkalinity are observed, showing that fermented waste has not been reacted. Gas ingredient which determined by GC has been compared with ingredients of gases produced by pyrolysis and fermentation, but no great changes have been observed gas ingredients of fermented waste samples which 10, 20 and 30 L gas transferred within. Only a 3 % increase in H_2 amount has been observed by increasing gas amount which Transferred within fermented waste.

4. Discussion and Conclusion

In this article, a biological tar treatment method developed using raw material as cattle fertilizer hybrid with pyrolysis. In recent years new technologies have been developed on biomass energy. However, there is insufficient work on tar remediation technologies. In this study, a brand-new treatment method which has never witnessed in literature before is studied. By this technique easier and cheaper treatment of tar pollutants within synthesis gas is intended. Tar treatment is achieved about 56 % and no gas outcome from fermented waste is observed. These studies on removal tar systems should be improved and methods should be developed for production of high-quality tar-free synthesis gas production. Because it has some advantages such as eco-friendly structure and high yield. The tar components have not been created an inhibitory effect in the system, as they react with the cattle fertilizer and continue the gas outlet process. In this study, the tar conversion efficiency remains at 56% and the system has been operated as a batch. To reach higher efficiencies, it will be appropriate to develop the system as a continuous system in the next studies.

Author Contributions

In this article, Ahmet ERYŞAR proposed the concept and subject, designed the research and experiments, reviewed the manuscript. Pınar BÜYÜK jointly conceptualized the paper, developed the methodology, made experiment, wrote the manuscript, and discussed the results.

Conflict of Interest

There is no conflict of interest.

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