

Kinetic analysis of thermochemical processes for dried cattle dung

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Summary

Cattle dung is a lignocellulosic material with high moisture and high ash content, which has the potential of energy generation or conversion. Currently, for energy conversion it is utilized in anaerobic digestion and direct combustion process. Anaerobic digestion generates biogas but has a low carbon conversion efficiency, and requires removal of hydrogen sulfide and ammonia from the biogas before use. Direct combustion is only used in developing countries as cheap energy resources for cooking and heating purposes in low efficiency stoves which causes many chronic respiratory diseases and deaths due to poor indoor air quality. Cattle dung is a cheap source of fuel which can be utilized in various thermochemical conversions to convert it into various solid, liquid and gaseous fuels, which are more efficient and high in energy density. As, the fuel has to be dried for thermochemical conversion, dried cattle dung is used for experiments.

In this thesis, the kinetics of three major types of thermochemical processes; pyrolysis, combustion and gasification (partial oxidation) is studied. Ultimate and proximate analysis of dried dung is performed to predict behavior of fuel. Thermo gravimetric (TG), Differential Thermo gravimetric (DTG) and Differential Scanning Calorimetry (DSC) techniques are used to understand effect of heat rate and flow rate in thermochemical conversion processes. Cattle dung ash that results from the thermochemical processes contains a high amount of mineral matter, majorly silica. It contains various plant nutrition elements like phosphorus (P), potassium (K), magnesium (Mg), sodium (Na) etc. Phosphorus and potassium being a major element for plant development, an experiment is performed to estimate the elemental P and K content in ash. From the experimental content, usage of ash is discussed.

1. Introduction

Biomass can be defined as any general hydrocarbon material which can be obtained from biodiversity. For political and social reasons, other materials such as tires, manufactured from either synthetic or natural rubbers may be included under the category of biomass even though the material is not strictly biogenic but considered into municipal solid waste or other waste. [1, 2] Biomass contains high volatile matter that can be transformed to other gaseous and liquid fuels through thermochemical processes like pyrolysis, gasification and combustion.

Pyrolysis is simply decay of the initial solid fuel into gases and liquids without an oxidizing agent in presence of high heat. The process of pyrolysis of biomass is very complicated and consists of both concurrent and successive reactions when

biomass is heated in a non-reactive atmosphere. In this process, thermal decay of organic components in biomass starts at 350 °C–550 °C and goes up to 700 °C–800 °C in the absence of air/oxygen [4]. The long chains of carbon, hydrogen and oxygen compounds in biomass crack into smaller molecules in the form of gases, condensable vapors (tars and oils) and solid charcoal under pyrolysis conditions. Rate and extent of decomposition of each of these components depends on reactor (pyrolysis) temperature, biomass heating rate, pressure, reactor configuration, feedstock etc. Process parameters. [3] Combustion is an exothermic reaction between hydrocarbon and oxygen in biomass. After complete combustion, biomass is converted to H₂O and CO₂.

The production of generator gas (alias producer gas and syngas) through gasification process is partial oxidation of biomass and takes place at temperatures of about 1000 °C.

The reactor is called a Gasifier. [5] In gasification where conditions are sub-stoichiometric, there is a surplus of solid fuel (incomplete combustion) the products of combustion are combustible gases like Carbon monoxide (CO), Hydrogen (H₂) and traces of Methane and non-useful products like tar and dust. The production of these gases is by reaction of water vapor and carbon dioxide through a glowing layer of charcoal. Thus the key to Gasifier design is to create conditions such that biomass is reduced to charcoal and charcoal is converted at suitable temperature to produce CO and H₂. [6]

2. Motivation

2.1 Cattle Manure as Source of Energy

Emission from cattle manure consists in total 25% of total emission from agriculture, which consists of 12% of global GHG emission. So, directly animal manure consists of 3% of global GHG emissions. This GHG emission can be reduced by proper management and usage of manure.

As received cattle manure is composed of undigested lignocellulose material, moisture (20-70%) and ash (15-20% dry basis). Lignocellulose present in manure is undigested feed to cattle. Manure contains methanogen bacteria that continuously decomposes lignocellulose into methane and carbon dioxide. If manure is not handled properly, greenhouse gases like methane and carbon dioxide gets emitted into atmosphere.

Presently, cattle manure is utilized for energy purposes in two ways:

1. Anaerobic Digestion
2. Direct Combustion

2.2 Indoor air pollution due to combustion of dried dung

Indoor air pollution is the degradation of indoor air quality by harmful chemicals and other materials. In developing countries, comparatively level of indoor air pollution is higher due to usage of lower grade biomass as fuel for cooking and heating. Indoor air pollution from solid fuels accounted for 3.5 million deaths and 4.5% global daily-adjusted life year in 2010; it also accounted for 16% particulate matter pollution. [7]

Dried dung is popular fuel for cooking and heating purposes in developing countries. Direct combustion of this fuel degrades indoor air quality. Amongst all general woody biomass, dried dung causes maximum amount of indoor air pollution. [8]

2.3 Dried Cattle dung as feedstock for thermochemical process and analysis of ash

Dried cattle dung's thermochemical conversion has not been studied much due to the popularity of anaerobic digestion process. Also, to cope with indoor air pollution from combustion of dried dung, study of thermochemical processes is necessary. So, in this thesis, analysis of various kinetic parameters of pyrolysis, combustion and gasification is studied. Also, dried cattle dung ash contains significant amount of phosphorus and potassium which is essential plant feed. So, analysis of ash is also done to find out phosphorus and potassium content.

3. Fuel Analysis

Thermal design of a biomass energy systems necessarily needs the composition of the fuel as well as its energy content. The following three primary properties describe its composition and energy content: (1) ultimate analysis, (2) proximate analysis, and (3) heating values.

3.1 Ultimate Analysis

Here, the composition of the biomass fuel is expressed in terms of its basic elements except for its moisture (M) and inorganic constituents (ASH). A typical ultimate analysis is

$$C + H + O + N + S + ASH + M = 100\% \quad (1)$$

Here, C, H, O, N, and S are the weight percentages of carbon, hydrogen, oxygen, nitrogen, and sulfur, respectively, in the fuel. Not all fuels contain all of these elements. The moisture or water in the fuel is expressed separately as M. Thus, hydrogen or oxygen in the ultimate analysis includes hydrogen and oxygen present in the organic components of the fuel.

3.2 Proximate Analysis

Proximate analysis gives the composition of the biomass in terms of gross components such as moisture (M), volatile matter (VM), ash (ASH), and fixed carbon (FC). The moisture and ash determined in proximate analysis refer to the same moisture and ash determined in ultimate analysis. The volatile matter of a fuel is condensable and non-condensable vapor released when the fuel is heated. Fixed carbon is solid carbon in the biomass that remains in the char in the pyrolysis process after devolatilization. Summation of all the content present by weight percentages in proximate analysis must be 100%.

3.3 Higher Heating Value

Higher calorific value (HCV) is defined as the amount of heat released by the unit mass or volume of fuel (initially at 25 °C)

once it is combusted and the products have returned to a temperature of 25 °C. It includes the latent heat of vaporization of water.

To find HCV from ultimate analysis of fuel, CY Yin has suggested following equation (1.9) of Channiwala and Parikh [9]. Equation is on dry basis which doesn't account for inherited moisture. With help of linear regression analysis, equation (1.9) has comparatively low mean absolute error. [10]

$$HCV \left(\frac{MJ}{kg} \right) = 0.3491C + 1.1783H + 0.1005S - 0.1034O - 0.0151N - 0.0211 \quad (2)$$

* Ash

3.4 Lower Heating Value

The lower calorific value (LCV) is defined as the amount of heat released by fully combusting a specified quantity without considering the heat of vaporization of the water in the combustion product. To calculate LCV from HCV following equation (1.10) is used. Enthalpy of evaporation of water at 25 °C is 2.442 MJ/kg.

$$LCV \left(\frac{MJ}{kg} \right) = HCV - (9 * H \quad (3)$$

* Enthalpy of evaporation)

To know about characteristics of fuel, knowledge of fuel composition is necessary. For that, proximate and ultimate analysis of fuel is carried out. Proximate analysis was done using TG characteristic graphs and ultimate analysis is done using gas chromatography of flue gas from fuel.

3.5 Results

As the fuel quantity used in equipment was around 10 milligrams and that content of fuel can be non-homogeneous in nature, so for that five reproducibility experiments were done. Average result of five experiments are shown in table 1.

Table 1 Proximate Analysis of Dung cake

Parameter	Average values
Moisture (%)	5.01
Volatile Matter (%)	66.11
Fixed Carbon (%)	13.83
Ash (%)	15.04
Total	100

This method is not a standard method. It is performed to have an approximate measurement of all the entities of proximate analysis.

Ultimate analysis is elemental analysis of fuel. It was carried out in fuel research laboratory at IST, Lisbon using their indigenous methodology M.M. 8.6 (A.E) (2009-05-06) and using Fisons Instrument EA 1108 instrument. First, the fuel is combusted and then amount of C, H, N, S are analyzed using gas chromatography of flue gases. Analysis was performed three times and average of the three values are taken as final result. Result of the ultimate analysis is shown in table 2.

Table 2 Ultimate Analysis of Dung cake

	As Received (%)
N	1.573
C	38.95
H	5.05
O	34.36
S	<2%
Moisture	5.013
Ash	15.04
HCV ^a (kJ/kg)	15.65
LCV ^a (kJ/kg)	14.31

*a = dry basis

4. Thermal Analysis of Dried Dung

4.1 Sample Preparation

Dung cakes used in experiment collected from site and dried in heat of Sun. When it gets dry, it is collected and used as fuel. As, in TGA and DSC analysis, sample used is in small quantity; it has to be ground to fine particles. Dung cake is ground using mortar and pestle until it was fine grain.

4.2 Equipment

TA Instruments SDT 2960 Simultaneous DSC-TGA

Equipment contains a standard furnace, which can be heated 1500° C. However, the highest temperature that samples were heated, is to avoid burnout of the furnace. The heating rates used ranged from 0.1 °C/min to 100 °C/min. A cooling of the crucibles used for experiment is done by instrument air which is forced inside the furnace. Aluminum Oxide crucibles were used for loading the samples. Equipment is linked to a computer installed with TA Instruments software, which was used to control the equipment and display the results of the experiments. Simultaneous DSC-TGA measures both the heat flows (DSC) and weight changes (TGA) associated with transitions in a material as a function of temperature and time in a controlled atmosphere.

4.3 Pyrolysis

Procedure

Initially, around 10 mg of sample is taken into alumina pan roughly measured in weighing machine. First, equipment has to be tarred for the weight and energy balance for DTG and DSC signal and then programming for the experiment in equipment was done. Pyrolysis was done at four different heat rates 5, 20, 50, 100 °C/min, from initial temperature 40 °C to 800 °C. Isothermal time maintained at 800 °C is 60 minutes for higher heat rates and 10 minutes for lower heat rates. Char combustion after every pyrolysis experiment was done with same condition i.e. heat rate 20 °C/min and isothermal for 30 minutes at 800 °C. For inert medium in furnace, nitrogen is used at constant flow rate of 50 ml/min and for combustion, air is used at 50 ml/min for all the experiments done.

Kinetic Analysis

From figure 1, it is noticed that there are three stages of mass losses, first from 40 °C to 200 °C, second from 200 °C to 350 °C and third in the end till 800 °C. This shows that there are three types of materials present in the sample. First stage can be explained by presence of moisture that evaporates till sample reaches 200 °C.

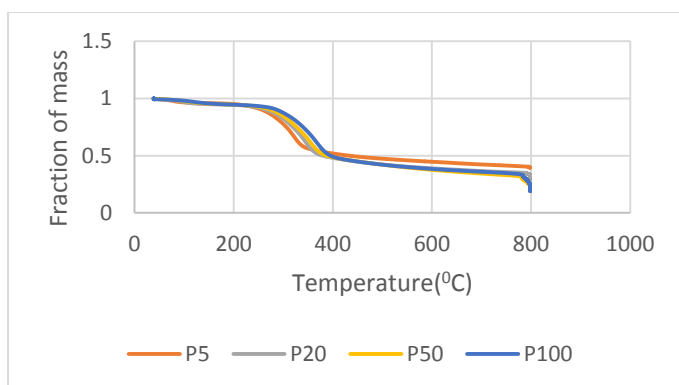


FIGURE 1 PYROLYSIS OF DUNG CAKE AT DIFFERENT HEAT RATE

As, dung cakes are Lignocellulosic materials, second and third stage is decomposition of the presence of Lignocellulosic materials. Second stage can be explained by the presence of cellulose and hemicellulose and third stage can be explained by presence of lignin. [11]

Effect of heat rate on volatile matter (VM) produced during pyrolysis

Here, effect of heat rate on char production was studied by S. Katyal et al. heating rate influences the rate of volatile evolution from the biomass. The higher heating rate above 400°C promotes rapid volatile evolution. The molecular

disruption is extremely fast and volatile fragments are released so rapidly that successive adjustments and equilibrium leading to further primary reactions that yield char have less opportunity to take place. [12] As the heat rate increases amount of volatiles released increases.

DSC curves of dung cake is shown in figure 2 with exothermic values as positive. Initial deep from 40 °C to 200 °C is due to moisture evaporation which is endothermic reaction. Heat released during pyrolysis of biomass can be explained by decomposition of the Lignocellulosic structure of biomass. At higher temperatures (above 500 °C) , anhydrosugar compounds in cellulose and hemicellulose undergo fission, dehydration, disproportionation and decarboxylation reactions to provide a mixture of low molecular weight gaseous and volatile products.

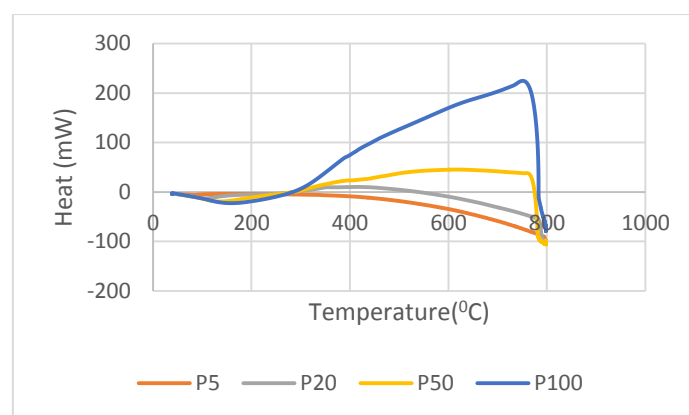


FIGURE 2 DSC CURVES OF DUNG CAKE PYROLYSIS AT DIFFERENT HEAT RATES

Effect of heat rate on char produced during pyrolysis

Here, amount of char produced after each pyrolysis process is found out by combustion of char because char produced contains generally two entities, fixed carbon and ash. Only Char is combustible, so in the end of combustion operation ash will be left.

With increase in heat rate, amount of char produced after pyrolysis decreases. This result can also be verified with DSC curves. As, the quantity of char increases, amount of heat released during the combustion process will also increase. This is shown in figure 3.

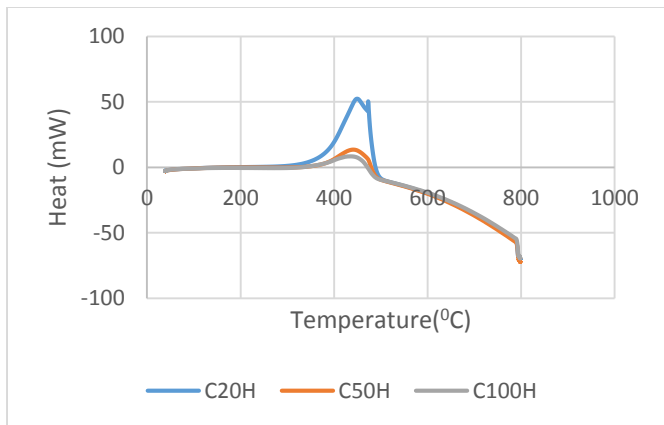


FIGURE 3 DSC CURVES OF COMBUSTION OF CHAR

Char Characteristics

Char is a high calorific value product of pyrolysis. It contains high amount of carbon. The most important characteristic temperatures of a combustion profile are ignition temperature and peak temperature. The ignition temperature corresponds to the point at which the burning profile undergoes a sudden rise. The ignition temperatures of samples are determined from their burning profiles. The point on the burning profile at which is the rate of weight loss due to combustion is maximum known as peak temperature. [13] Here, ignition temperature of char derived from dung cake is 298 °C and peak temperature is 418 °C.

4.4 Combustion

Procedure

Initially, around 10 mg of sample is taken into alumina pan roughly measured in weighing machine. First, equipment has to be tarred for the weight and energy balance for DTG and DSC signal and then programming for the experiment in equipment is to be done. Combustion was done at four different heat rates 5, 20, 50, 100 °C/min, from initial temperature 40 °C to 800 °C. Isothermal time maintained at 800 °C for 30 minutes for higher heat rates and 10 minutes for lower heat rates. Air flow in the furnace is 50 ml/min and it is maintained constant for all the experiments.

Kinetic Analysis:

Kinetic study of combustion of biomass was studied by Haykırı-Açma Hanzade. When biomass is combusted in the beginning moisture is released. Then combustion of volatile matter and carbonization of fixed carbon occurs and then combustion of carbonized char occurs. This three phenomenon was observed from DTG curves. [14]

As discussed, to study combustion of biomass; DTG curves are useful. DTG curve of combustion of dung cake at 5 °C/min heat rate is shown in figure 4. In this figure, three different types of peak is visible. In the beginning, first peak of mass loss shows evaporation of moisture. Then, second peak is the

combustion of volatile matter which starts at 180 °C and ends at 400 °C. Third peak between 430 °C to 500 °C shows combustion of carbonized char.

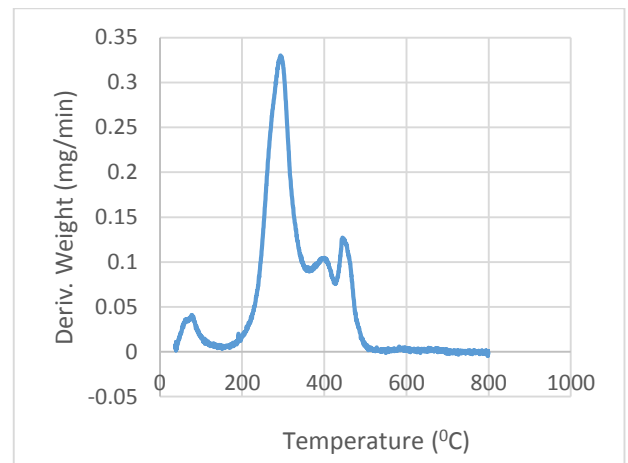


FIGURE 4 DTG CURVE OF COMBUSTION OF DUNG CAKE

Now, heat rate is increased from 5 °C/min to 100 °C/min. From figure 5, it is seen that as heat rate increases, ignition temperature, peak combustion rate and peak temperature increases. The rate of weight loss at combustion profile peak temperature is called the maximum combustion rate. Also, carbonized char content decreases as the heat rate increases. That is the reason that third peak in combustion at 100 °C/min is very low.

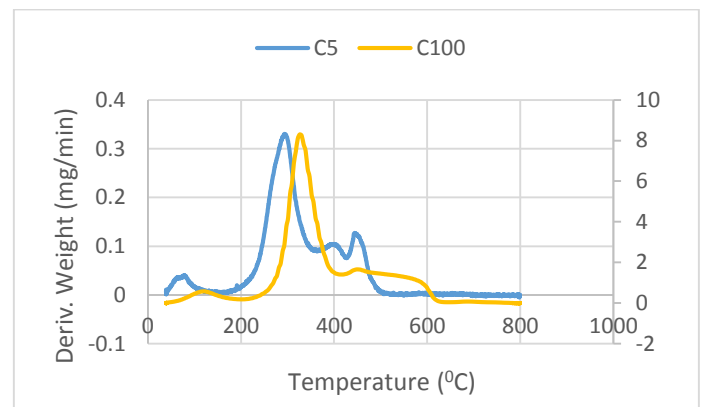


FIGURE 5 DSC CURVES AT DIFFERENT HEAT RATES

4.5 Partial Oxidation

Procedure

Initially, around 10 mg of sample is taken into alumina pan roughly measured in weighing machine. First, equipment has to be tarred for the weight and energy balance for DTG and DSC signal and then programming for the experiment in equipment is to be done. For partial combustion, six experiments with same heat rate and different oxygen content are done. For partial oxidation, air quantity is varied from complete combustion (50 ml/min of air) to pyrolysis (no air).

Total flow in the furnace is 50 ml/min and it is maintained constant for all the experiments.

Kinetic Analysis

Kinetic study of partial oxidation of lignocellulosic biomass was studied by Amutio Maider et al. As oxygen supplied to biomass decreases during different oxidation experiments, ignition temperature, peak temperature increases and peak combustion rate decreases. [15]

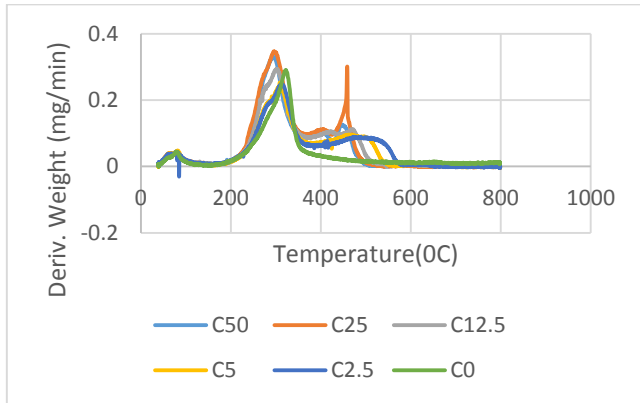


FIGURE 6 DTG CURVES OF PARTIAL OXIDATION OF DUNG CAKE

As it is noticeable from figure 6, as amount of oxygen decreases, third peak is getting flatter. This means amount of fixed carbon that was burning during higher air supply is now converted into char. It is visible that as air supply decreases ignition temperature and peak temperature increases and peak combustion rate decreases.

DSC curves of partial oxidation of dung cake at different air supply rates are shown in Figure 7. Graph is between heat supplied/released (mW) to time (min). So, area under curve indicates total heat released during the oxidation process. In the figure, we can see two peaks, first being combustion of volatiles and second being combustion of char. As, oxygen content decreases, amount of heat released decreases.

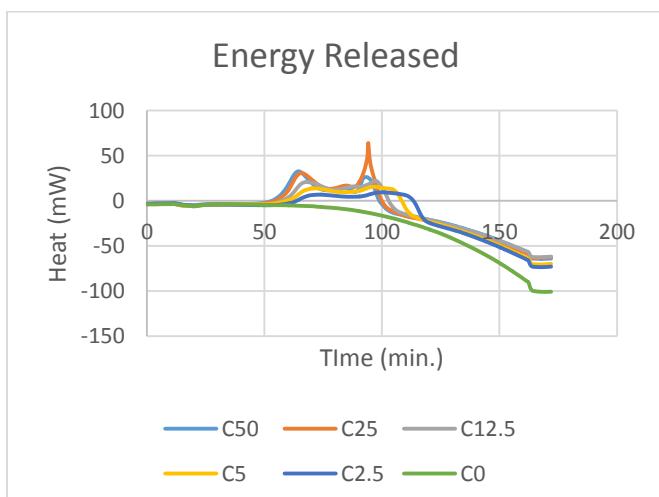


FIGURE 7 DSC CURVES OF PARTIAL OXIDATION OF DUNG CAKE

5. Kinetic Modelling

5.1 Kinetic Model for Pyrolysis

As discussed earlier, during pyrolysis process all the moisture and volatile matter in the fuel sample evaporates and in the end only char and ash remains as it is. [15]

Three major components of lignocellulosic biomass; hemicellulose, cellulose and lignin has significant role in pyrolysis of biomass sample. Cellulose and hemicellulose contains high amount of volatile matter and very low fixed carbon and lignin contains very low volatile matter and high amount of fixed carbon. This simplifies pyrolysis of lignocellulosic materials.

For kinetic modelling, pseudo component modelling method is used. Total material mass at any time in process is divided between four pseudo components of biomass; moisture, hemicellulose; cellulose, lignin. Ash is the residual component which remains fixed always. During pyrolysis process, part of lignocellulose that gets converted to char is also accounted into ash while modelling.

Equations related to modelling

Before starting about model, discussion of equations used is necessary. From the Arrhenius equation shown as

$$k = A e^{\frac{-E_a}{RT}} \quad (4)$$

In this equation terms which are temperature dependent are rate constant k. Frequency factor A, activation energy E_a and universal gas constant R do not vary much with respect to change in temperature.

Imagine, if we want to measure rate constant and activation energy at temperature $T_0 = 300^\circ\text{C}$ (573 K) then value of k will change. Considering T at 300°C as reference value then value of temperature and rate constant at reference value would be T_{ref} and k_{ref} and equation (4) can be modified as:

$$k_{ref} = A * e^{\frac{-E_a}{R * T_{ref}}} \quad (5)$$

Now, dividing equation (4) by equation (5) and after simplification we get,

$$k(T) = k_{ref} * e^{\frac{-E_a}{R} \left[\frac{1}{T} - \frac{1}{T_{ref}} \right]} \quad (6)$$

Considering all the reactions occurring with pseudo components as first order reactions, rate of reaction can be written as,

$$\frac{dW}{dt} = k(T) * W \quad (7)$$

Where, W is the weight of pseudo component at time t and k (T) is rate constant at temperature T. Now, quantity of pseudo component at any time can be found out by using Euler's method for solution of first order differential equation. Therefore, quantity of pseudo component at time t can be written as,

$$W_1 = W_0 + \frac{dW}{dt} * (t - t_0) \quad (8)$$

Where W_0 is the weight of sample at time t_0 . Time step ($t - t_0$) is 0.001 second.

Model

Initially thermo gravimetric analysis was performed on dung cake at different heat rates (5, 20, 50, 100 °C/min) with nitrogen. For pseudo component model, every component (moisture, hemicellulose; cellulose, lignin) was assigned initial value (later on taken as variable value) and using equation (6) their rate constants were found at any time t. After finding rate constant rate of each pseudo component was found out by using equation (7). From rate of reaction, pseudo weight was found out by using equation (8). At any time t, summation of mass of every pseudo component with dead mass of ash will give amount of matter left in pan in analyzer. Total modelled weight W_{model} of sample at any time t during process will be,

$$W_{moi} + W_{hemi} + W_{cell} + W_{lig} + W_{ash} = W_{model} \quad (9)$$

Where, W_{moi} is moisture content, W_{hemi} is hemicellulose content, W_{cell} is cellulose content, W_{lig} is lignin content, W_{ash} is ash content, and W_{model} is total weight of sample at any time t.

Modelling is done using excel solver program. In which first objective function has to be set up. In this model objective function is taken as summation of square of error (difference of practical weight $W_{practical}$ and modelled weight) at different heat rates. Objective function is shown as,

$$O.F. = \sum_{i=1}^4 * \sum_{j=1}^N (W_{practical} - W_{model})^2 \quad (10)$$

Where, j = 1,2..., N is the total no. of steps in the experiments and j=1,2,3 and 4 are values of total square of error at heat rates of 5, 20, 50 and 100 °C/min respectively.

Results

The activation energies for the pyrolysis of the different pseudo components are shown in table 3. From the experiments of J. J. Orfão et al. of pyrolysis of different components of lignocellulosic biomass it can be concluded that while pyrolyzing biomass initially moisture evaporates followed by destruction of hemicellulose, cellulose and lignin structure destruction [52].

Table 3 Activation energies estimated for the pyrolysis of the different pseudo components considered.

	Hemicellulose	Cellulose	Lignin	Moisture
k(300) (1/min)	0.62	0.07	0.01	22.48
Ea (kcal/mol)	18.04	24.98	5.53	9.46

High values of k(300) and activation energy Ea suggests that hemicellulose will decompose at lower temperatures and lower values of k(300) and Ea suggests that lignin will decompose in wide range of temperature. Whereas, cellulose will have higher peak because of high value of Ea and decompose after hemicellulose because of lower value of k(300).

5.2 Kinetic Model for Combustion

Model

Experiments were performed at four different heat rates (5, 20, 50 and 100 °C/min) using same amount of air flow (50 ml/min) from initial temperature of 40 °C to 800 °C. Kinetic modelling of combustion process is similar to modelling of pyrolysis. All the equations (equations (6) to (10)) and process mentioned in modelling of pyrolysis is used in the same manner except for equation (7). Equation (7) has to be modified to account for combustion. Equation (11) is the modified equation which has an extra component multiplied i.e. partial pressure of oxygen which is constant for all experiments $p_{O_2}=0.21$ atm. [61]

$$\frac{dW}{dt} = k(T) * W * p_{O_2} \quad (11)$$

Results

Activation energies of pseudo components are shown in table 4. From the experiments of J. J. Orfão of combustion of different components of lignocellulosic biomass it can be deduced that while combusting biomass initially moisture evaporates followed by combustion of hemicellulose, cellulose (volatiles) and lignin (char) structure. [16]

Table 4 Activation energies of pseudo components

	Hemicellulose	Cellulose	Lignin	Moisture
k(300) (1/min)	0.52	0.18	0.01	43.15
Ea (kcal/mol)	20.42	24.69	19.7	9.48

5.3 Kinetic Model for Partial Oxidation

Model

Here, main assumption considered during modelling is that partial oxidation is considered as mixture of pyrolysis and combustion. Three pseudo lignocellulosic components will have fraction of pyrolyzable material and fraction of combustible material. As, discussed by Amutio, Maider, et al, while modelling it is assumed that pyrolyzable fraction of the pseudo component has same activation energy and k(300) as of pyrolysis process and non pyrolyzable (combustible) fraction has same activation energy and k(300) as of combustion process.

Kinetic modelling of partial oxidation is similar to modelling of pyrolysis and combustion but equations used for it will be modified for partial oxidation. Equation (7) is modified to accommodate dual effect of pyrolysis and combustion as below,

$$\frac{dW}{dt} = -k(T)_C * W * r - k(T)_P * W \quad (12)$$

Where k (T)_C, k (T)_P and r for all pseudo components are computed with help of following equations,

$$k(T)_C = k(300)_C * e^{\frac{(-E_a)_C}{R} \left[\frac{1}{T} - \frac{1}{T_{ref}} \right]} \quad (13)$$

$$k(T)_P = k(300)_P * e^{\frac{(-E_a)_P}{R} \left[\frac{1}{T} - \frac{1}{T_{ref}} \right]} \quad (14)$$

$$r = \frac{p^{O_2}}{p^{O_2} + k} \quad (15)$$

Where, (Ea)_C and (Ea)_P are activation energies associated with combustion and pyrolysis respectively. T_{ref}=300°C and W is weight of pseudo component and T is temperature at any step of experiment. k (300)_C and k(300)_P are rate constant at reference temperature associated with combustion and pyrolysis respectively. R is gas constant. k is adsorption constant included for Langmuir adsorption. Two portions pyrolyzable and non pyrolyzable content combined in equation (12). As mentioned before, for all pseudo components, value of activation energy Ea and k(300) is taken as same as obtained in pyrolysis and combustion counterpart.

So, variables left in the process are initial values of pseudo components W₀₁, W₀₂, W₀₃ and W₀₄ respectively for moisture, hemicellulose, cellulose and lignin and Langmuir adsorption coefficient k.

Moisture does not have any effect on partial pressure of oxygen. Only thing affects evaporation of moisture is temperature. So, values of kinetic parameters of moisture for partial oxidation are taken as same of combustion as it has lower values of error.

Results

At higher partial pressure, amount of O₂ is high. So, combustion parameters will dominate the process at higher partial pressure and pyrolysis parameters will dominate at lower partial pressure. Value of k from modelling is found out as 0.3 atm.

6. Ash Analysis

6.1 Introduction

Cattle manure is the oldest fertilizer that human being is still using for farming. But now, use of cattle manure in farms is a popular practice in only few rural areas. This type of manure is not as rich in nitrogen as many other type of fertilizer, also high ammonia levels can burn plants when the fresh manure is directly applied. For this reason, it's usually aged or composted prior to its use as cow manure fertilizer. Composting manure eliminates harmful ammonia gas, pathogens and weed seeds. Cattle manure is basically made up of digested grass and grain. Cow dung is high in organic materials and rich in nutrients. It contains about 3% nitrogen (N), 2% phosphorus (P), and 1% potassium (K) (3-2-1 NPK). [17]

6.2 P and K analysis

Methodology

Ash used in analysis was collected from combustion of feedlot manure. Approximately 40 mg of ash was used in the analysis. The method used for analysis is inductively coupled plasma atomic emission spectroscopy (ICP-AES), also referred to as inductively coupled plasma optical emission spectrometry (ICP-OES), a trace metal element analysis method. Trace metal analysis shows amount of metal present in the sample.

Result

Result is presented as percentage of P and K in total ash content: Phosphorus as metal element is 3.1% and Potassium is 6.5%.

Conclusions

Thermal Analysis

1) Pyrolysis

From TG curves of pyrolysis of dried cattle dung, three different types of reactions were observed due to three different slopes in TG curve i.e. i) Evaporation of moisture (from 40 °C to 200 °C) ii) decomposition and evaporation of pyrolyzable matter from cellulose and hemicellulose (from 200 °C to 400 °C) and iii) decomposition and evaporation of pyrolyzable matter from lignin (from 400 °C to 800 °C).

Higher the heat rate during pyrolysis process, lower the char content and higher volatile matter and vice versa. As heat rate increases, heat release rate from fuel also increases because of fission, dehydration, disproportionation and decarboxylation reactions of polysaccharides compounds present in hemicellulose and cellulose. Ignition temperature of char obtained from pyrolysis of dung cake is 298 °C and peak temperature is 418 °C.

2) Combustion

From DTG curves of combustion of dried cattle dung, three different types of reactions were observed due to three different peaks in DTG curve i.e. i) Evaporation of moisture (from 40 °C to 180 °C) ii) combustion of volatile matter and char reduction (from 180 °C to 400 °C) and iii) combustion of char (from 400 °C to 500 °C).

As heat rate increases, ignition temperature, peak temperature and peak combustion rate increases and because of this shift or delay, combustion of char also falls in that regime of temperature. Thus, combustion of char is not well observed during combustion at 100 °C/min.

3) Partial Oxidation

As oxygen supplied to biomass decreases during different oxidation experiments, ignition temperature, peak temperature increases and peak combustion rate decreases because lack of oxygen causes ignition delay and delays combustion process.

When partial pressure of oxygen decreases, char combustion rate decreases and maximum char combustion temperature increases.

As oxygen content decreases, amount of heat released from sample decreases. This can be explained by Lower oxygen supply causes production of CO instead of CO₂ which has lower.

Kinetic Modelling

Comparison of activation energy, rate constant at reference temperature and error associated with modelling is shown in table 5. Only significance difference is in parameters of pyrolysis and combustion of lignin. The third peak of char combustion during combustion of dried dung explains higher value of activation energy Ea and rate constant at reference temperature k(300) compared to that obtained by pyrolysis. Activation energy of moisture in both cases are same. Error associated with modelling of pyrolysis is higher compared to modelling of combustion. Value of Langmuir constant (k) obtained through modelling of partial oxidation process is 0.3 atm.

Table 5 Comparison of Kinetic parameters of pyrolysis and combustion

Process	Pseudo Component	k(300) (1/min)	Ea (kcal/mo l)
Pyrolysis	Hemicellulose	0.62	18.05
	Cellulose	0.073	24.98
	Lignin	0.0067	5.53
	Moisture	22.48	9.47
Combustion	Hemicellulose	0.52	20.43
	Cellulose	0.18	24.7
	Lignin	0.01	19.76
	Moisture	43.14	9.49

Ash Analysis

Values of phosphorus and potassium obtained from elemental analysis of ash are 3.1 % and 6.5 % which is very significant for its usage as fertilizer. This ash can be used as direct fertilizer to legumes plant, to be made as perfect fertilizer by mixing it with nitrogen containing solutions like animal urine or recovery of phosphorus and potassium from ash through various processes and utilize it to make synthetic fertilizer. [18, 19, 20]

References

1. Hall, D. O., Rosillo-Calle, F., Woods, J., & Williams, R. H. (1993). Biomass for energy: supply prospects.
2. Klass, D. L. (1998). Biomass for renewable energy, fuels, and chemicals. Academic press.
3. Jahirul, M. I., Rasul, M. G., Chowdhury, A. A., & Ashwath, N. (2012). Biofuels production through biomass pyrolysis—a technological review. *Energies*, 5(12), 4952-5001.
4. Fisher, T., Hajaligol, M., Waymack, B., & Kellogg, D. (2002). Pyrolysis behavior and kinetics of biomass derived materials. *Journal of analytical and applied pyrolysis*, 62(2), 331-349.

5. Basu, P. (2010). Biomass gasification and pyrolysis: practical design and theory. Academic press.
6. Cornelissen, T., Yperman, J., Reggers, G., Schreurs, S., & Carleer, R. (2008). Flash co-pyrolysis of biomass with polylactic acid. Part 1: Influence on bio-oil yield and heating value. *Fuel*, 87(7), 1031-1041.
7. Kankaria, A., Nongkynrih, B., & Gupta, S. K. (2014). Indoor air pollution in India: Implications on health and its control. *Indian journal of community medicine: official publication of Indian Association of Preventive & Social Medicine*, 39(4), 203.
8. Kandpal, J. B., Maheshwari, R. C., & Kandpal, T. C. (1995). Indoor air pollution from combustion of wood and dung cake and their processed fuels in domestic cookstoves. *Energy conversion and management*, 36(11), 1073-1079.
9. Yin, C. Y. (2011). Prediction of higher heating values of biomass from proximate and ultimate analyses. *Fuel*, 90(3), 1128-1132.
10. Dasappa, S. (2014). Thermochemical Conversion of Biomass. *Transformation of Biomass: Theory to Practice*, 133-157.
11. Yang, H., Yan, R., Chen, H., Lee, D. H., & Zheng, C. (2007). Characteristics of hemicellulose, cellulose and lignin pyrolysis. *Fuel*, 86(12), 1781-1788.
12. Katyal, S., Thambimuthu, K., & Valix, M. (2003). Carbonisation of bagasse in a fixed bed reactor: influence of process variables on char yield and characteristics. *Renewable Energy*, 28(5), 713-725.
13. Demirbas, A. (2004). Combustion characteristics of different biomass fuels. *Progress in energy and combustion science*, 30(2), 219-230.
14. Haykırı-Açma, H. (2003). Combustion characteristics of different biomass materials. *Energy Conversion and Management*, 44(1), 155-162.
15. Amutio, M., Lopez, G., Aguado, R., Artetxe, M., Bilbao, J., & Olazar, M. (2012). Kinetic study of lignocellulosic biomass oxidative pyrolysis. *Fuel*, 95, 305-311.
16. Orfao, J. J. M., Antunes, F. J. A., & Figueiredo, J. L. (1999). Pyrolysis kinetics of lignocellulosic materials—three independent reactions model. *Fuel*, 78(3), 349-358.
17. Kirchmann, H., & Witter, E. (1992). Composition of fresh, aerobic and anaerobic farm animal dungs. *Bioresource technology*, 40(2), 137-142.
18. Ghosh, P. K., Bandyopadhyay, K. K., Manna, M. C., Mandal, K. G., Misra, A. K., & Hati, K. M. (2004). Comparative effectiveness of cattle manure, poultry manure, phosphocompost and fertilizer-NPK on three cropping systems in vertisols of semi-arid tropics. II. Dry matter yield, nodulation, chlorophyll content and enzyme activity. *Bioresource technology*, 95(1), 85-93.
19. Pradhan, S. K., Holopainen, J. K., & Heinonen-Tanski, H. (2009). Stored human urine supplemented with wood ash as fertilizer in tomato (*Solanum lycopersicum*) cultivation and its impacts on fruit yield and quality. *Journal of agricultural and food chemistry*, 57(16), 7612-7617.
20. Tan, Z., & Lagerkvist, A. (2011). Phosphorus recovery from the biomass ash: A review. *Renewable and Sustainable Energy Reviews*, 15(8), 3588-3602.