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A Review of Thermo-chemical Energy Conversion Process of Non-edible Seed Cakes

J. Thiagarajan, P.K. Srividhya, E. Rajasakeran

Department of Mechanical Engineering, Periyar Maniammai University, Vallam, Thanjavur, India

Corresponding Author email: srividya.aravazhi@gmail.com; Author

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Abstract In India, efforts were being made for using non-edible oils for production of bio-diesel on account of country's potentiality in non-edible oil tree born seeds. *Jatropha curcas* (Jatropha) and *Pongamia pinnata* (Karanja) crops had been selected as major source of non-edible oils for production of biodiesel. Considering the future scenario of non edible oil seed's utilization for biodiesel production, there is a need for efficient utilization of their cakes. The main focus of this review is about the options of energy conversions, for production of suitable fuel. The brief overview of energy conversion option on seed cake is presented by means of general background information available in literatures. From the solvent extracted jatropha seed cake and mechanically de oiled jatropha seed cake the quantity of biogas obtained by biomethanation process was 0.5 m^3/kg and 0.6 m^3/kg respectively with CH_4 content of 50% to 70%. By using pongaima seed cake as feed material the yield of average specific biogas over a 30-day retention time was 0.703 m^3•day^{-1}•kg^{-1} TS with 62.5% of CH_4 content. Faster conversion rate and using all the components of biomass includes cellulose, hemicelluloses and lignin were the advantages of thermo chemical conversion process over biological conversion process. Energy production through gasification conversion route is suitable as the process of synfuels from biomass will lower the energy cost, waste management improvement and reduction of harmful emission. Experiments on non edible oil seed cake by gasification conversion route and analyzing for its characteristics are more essential for useful energy recovery and its use for thermal application and power generation.

Keywords Non edible oil seeds; Bio diesel; De-oiled cake; Bio mass gasifier

Introduction

The universe has gifted with more than hundred species of tree born non edible oil seeds that could be used for extraction of oil which could be supplemented /substituted for the conventional fuel. India is emerging fast in using no edible oils for the production of bio diesel through B20 policy of bio fuel with conventional diesel (Radhakrishna, 2003). The table 1 shows the availability of non edible seeds, oil, cake and oil content in India. In that the Sal is 1.5 million metric tons per year followed by Neem, Mahua and Mango.

The trees and plants like Jatropha, Karanja, Rice-bran, Castor, Sal, Neem, Mahua, Linseed, rubber-seed etc could grow well on waste land and could withstand draught and dry conditions producing nontraditional oil seeds. Oil extraction from these seeds and conversion into bio diesel production provided opportunities for rural employment and wealth generation to the marginalize sections of the society (Agarwal et al., 2007). For making bio diesel techno economically as viable and renewable substitute or supplement to diesel certain barriers needed to be reviewed.

The technology of biodiesel production consumed only extracted vegetable oil from non-edible seeds and left large amount of unutilized biomass as seed cake.

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Table 1 Potential availability of non edible seeds in India (Radhakrishna P., 2003)

S.N.	General name	Botanical name	Potential, million metric tonnes/Year			Oil content%
			Seed	Oil	Cake	
1	Karanja*	*Pongamia pinnata*	0.20	0.055	0.145	27~39
2	Jatropha*	*Jatropha curcas*	0.05	0.015	0.035	30~40
3	Kusum	*Scheleichera oleosa*	0.08	0.025	0.055	34
4	Neem	*Azadirechta indica*	0.50	0.100	0.400	20
5	Pilu	*Salvadora oleoides*	0.05	0.017	0.033	33
6	Tumba	*Citrullus collocynthis*	0.10	0.021	0.079	21
7	Sal	*Shorea robusta*	1.50	0.180	1.320	12~13
8	Mahua	*Madhuca indica*	0.50	0.180	0.320	35
9	Mango	*Mangifera indica*	0.50	0.045	0.455	7.5

The disposal of generated cakes as waste led to environmental problems and indirectly effects cost for bio diesel production. The development of non edible oil seed plantations provided potential feed stock to biodiesel industry and also resulted in production of enormous quantities of seed cakes (Anonymous, 2012).

Normally the fruits of biodiesel resources were with 50% of seeds (kernels). Out of this maximum 35% could be converted into vegetable oil and the remainder gets rejected as toxic de-oxide seed cake. In fact 85% of cultivated bio- resource remained unutilized and 60 000 tones of jatropha de oiled cakes production had been estimated for 2007. The future scenario of the biodiesel production from the non edible oil seeds required extensive production of non edible oil seeds with time (Ram et al., 2009).

In this review a major focus was given on seed cakes of *Jatropha curcas* (Jatropha) and *Pongamia pinnata* (Karanja) as those two crops had been selected as major source of non-edible oil for production of biodiesel in India by massive plantation drive.

Jatropha and pongamia seed cake eneration

The extraction of jatropha oil for bio diesel production was done normally by crushing dried Jatropha curcas seeds as a whole in small scale screw press. The seeds including shells having an oil content of about 35% by weight and the oil extraction at most ranged between 25% to 30% by weight of the seeds (George, 2009). In the processing of jatropha seeds for oil production about 50% to 75% of the weight of seeds rendered as seed cake (Staubmann et al., 1997; Singh et al., 2008). In bio diesel industry depending upon the seed quality normally 3 tons of seed cake was generated per ton of bio diesel production (Mahajani, 2009). The content of the 9%~12% of oil by weight influenced gross energy value of seed cake approximately 18.2 MJ/kg (Achten et al., 2008). The total solids of the seed cake were volatile in nature and by obtaining one tone of seed cake per hectare represent about 18.2 GJ of energy (Jingura et al., 2010).

In case of pongaima tree yielding of seeds was about 10 to 15 tons per hectare with an average of 160 kg per year. The extraction was 0.25 kg of oil per kg of seed, leaving seed cake (Osman et al., 2009) with the calorific value of 14.3 MJ/kg (Raja et al., 2011). It was estimated that 0.056 million tons of pongaima seeds production against the potential of 0.20 million tons per year.

Figure 1 shows the composition of Jatropha and Pongaima Fruits. Out of 62.5% jatropha seeds around 25% to 30% of oil could be extracted and the remaining rendered as jatropha seed cakes. In case of pongaima fruit the seeds and shells were 50% of each and out of 50% of pongaima seeds the pongaima oil and seed cake generated were 35% and 65% respectively. The figure indicated that through oil extraction from these non edible seeds around 65% to 70% non edible seed cakes could be generated.

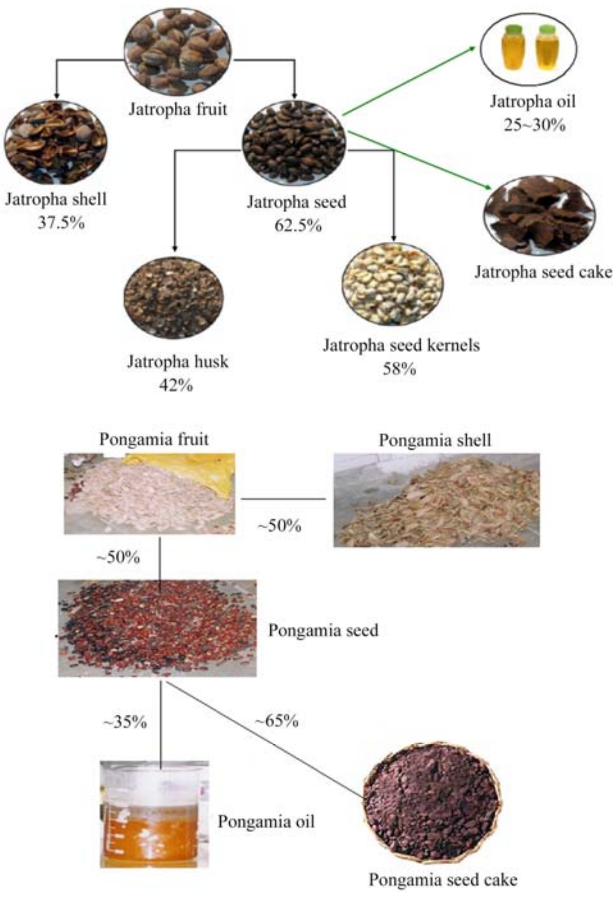

Figure 1 Composition of Jatropha and Pongamia fruit (Abreu, 2009; Subbarao, 2011)

Utilization of seed cake

The Jatropha seed cakes could not be utilized as animal/cattle feed as the shells of the seed contained phorbol esters and antinutrients such as trypsin inhibitor, lectin and phytate (Harinder et al., 2008) in case of pongaima deoiled cake number of toxic and unpalatable components, including the furanoflavones karanjin, pongamol, and other polyphenolic compounds were present (Mandal et al., 1985).

To utilize as a cattle feed the seed cakes needed to be detoxified by combination of heat treatment and solvent extraction processes which was not an economically viable option for commercial utilization (Mike, 2004).

Seed cake as a fertilizer

The conventional soil enrichment was one of the choices for utilization of seed cake because of high nitrogen content makes a valuable contribution nutrient requirement (Reyadh, 1997). Table 2 presented nutrient content of jatropha cake and pongaima cake. After composting the seed cake it could be used as fertilizer 1.0 kg of seed cake was equivalent to 0.15 kg of N:P:K (40:20:10) chemical fertilizer (Openshaw, 2000). The presence of oil at high level in the seed cake had negative effects with reduced the permeability of the soil (Jongh and Eric, 2010).

Table 2 Nutrient content of the de-oiled cake as a fertilizer

S.N.	Seed cake	N%	P%	K%	Source
1	Jatropha	4.4~6.5	2.1~3.0	0.6~0.7	Achten et al., 2008
		6.0	2.8	0.9	Del Greco and Rademaker, 1998
		3.0~4.5	0.65~1.2	0.8~1.4	Patolia, 2007
2	Pongamia	4.0	1.0	1.0	Meshram, 2010
		5.5	1.0	1.0	Ram et al., 2006
		4.0	0.9	1.3	Raja et al., 2011

Seed cake as a substrate for biogas generation

The self decomposition of seed cake in the open atmosphere by the action of various micro organisms generated the gases CH_4, N_2O, H_2S, NH_3 and CO_2 volatile organic compounds (VOCs) (Anonymous, 2012). The approach of using of non edible cakes as “Biomass” resources instead of disposing as “waste” made possible as to meet energy and economical benefits and also environmental benefits. The presence of carbohydrates and proteins subjected the non edible seed cake to anaerobic digestion, produced high calorific value of biogas (38 MJ/Nm3) and notably reduced gaseous emissions (CH_4, VOCs, H_2S) (Anonymous, 2012). Table 3 provided Biogas production potentiality of non edible seed cake.

The biogas generated from the non-edible seed cakes contained composition of methane 70% and remainder as carbon dioxide which was higher than the gas acquired from the cow dung based biogas plants

(Subbarao, 2003). In biomethanation the use of defatted cake as feed (combination of 75% cattle dung and 25% jatropha oil cake) provided best results (Nafisa et al., 2010). Groeneveld (2003) found that using mixture of seed cake and animal manure as feed sources in anaerobic process gave the composition of CH_4 in the generated biogas between 50% to 60% with yielding of 0.5 m^3/kg to 0.6 m^3/kg.

Table 3 Biogas production potentiality of non edible seed cake

S.N.	Feed stock	Gas yield (m^3/ kg dry)	Methane Content (%)	Methane yield (kg/m^3)	Source
1	Jatropha cake	0.598	66.6	0.394	Chandra et al., 2012
		0.446	70	-	Staubmann et al., 1997
		-	50~60	0.5~0.6	Groeneveld, 2007
		0.6	-		Radhakrishna, 2007
2	Pongamia cake	0.703	62.5	0.427	Chandra et al., 2012
3	Castor cake	0.4~0.5	70	-	Subbarao, 2003
4	Cow dung	0.18	55~60	-	Subbarao, 2003

Table 4 Chemical analysis of inlet and outlet slurry (Nafisa et al., 2010)

Biogas plant	Inlet slurry					Outlet slurry				
	Oil%	TS%	N%	P%	K%	Oil%	TS%	N%	P%	K%
Jatropha	5.67	10.76	3.51	2.06	0.66	3.95	8.87	5.56	2.90	1.24
Cow dung	-	9.64	0.54	0.49	0.51	-	7.22	1.42	1.04	1.02

Chandra et al. (2012) in their experiments on jatropha and pongamia pinnata de oiled seed cakes under mesophilic temperature condition observed that the yielding of about 0.593 $m^3 \cdot day^{-1} \cdot kg^{-1}$ TS from jatropha cake and 0.703 $m^3 \cdot day^{-1} \cdot kg^{-1}$ TS from pongamia seed cake over 30 days of retention time. In case of Jatropha the average content of CH_4 in the produced biogas was 66.5% at the dilution ratio of 3.5:1 and 62.5% with the dilution ratio of 3:1 for pongamia cake.

Staubman et al. (1997) obtained 0.446 m^3 of biogas containing 70% methane per kg of dry seed cake using pig manure as inoculums. Elsewhere, Radhakrishna (2007) obtained 0.5 m^3 biogas per kg of solvent extracted seed cake and 0.6 m^3 biogas per kg of mechanically de-oiled cake. Singh et al. (2008) observed that biogas production from Jatropha seed cake was about 60% higher than that from cattle dung and contained 66% methane. In India the potential of biogas generation was estimated to be 2 550 and 377 million cubic metre respectively from 10.2 to 1.45 lakh tones of jatropha and pongamia seed cakes (Ram et al., 2006).

The slurry from the bio gas plants of jatropha oil cake contained high NPK content than fresh jatropha oil cake, fresh cattle dung and its digested slurry (Table 4) and because of its high nutrient content could serve as good manure. The oil content also could be reduced from 5.67% to 3.95% (Nafisa et al., 2010).

The Table 4 indicated that compared to original feed material, the outcome slurry contained higher nitrogen and rich in minerals in concentrated form leads to use as manure. The anaerobic digestion method of biogas production led to good utilization of cakes for energy generation and the effluent could be used for organic farming (Anonymous, 2012). But, still there were certain limitations on energy generation from seed cake through anaerobic digestion, which were:

1. Biomethanation required powdery and porous biomass with moisture always greater than 60% (Kirubakarana et al., 2009). So the large quantity of water was to be disposed of after digestion.

2. The hydraulic retention time was always very high (45~60 days) for effective gas generation resulting in huge volume of digester.

3. When feed stock contained more of lignin, which was more stable in biodegradation process, then

biodigestion becomes difficult and conversion efficiency would be reduced. The seed cake was made up of the seed husk (42%) and kernel (58%) (Abreu, 2009) and seed husk had about 23.91% of lignin content (Viboon et al., 2007) that could not be completely converted into biogas in biomethanation process. The Table 5 stated the composition of Jatropha seed husk.

Table 5 Composition of Jatropha seed husk (Viboon et al., 2007)

S.N.	Composition	%
1	Cellulose	56.31
2	Hemi cellulose	17.47
3	Lignin	23.91

Thermo chemical conversion process

Thermo chemical conversion processes like combustion, pyrolysis and gasification were the best routes of biomass energy conversion. For agro waste management thermal processes were the best option for efficient utilization of energy conversion. Over biological conversion process the rate of conversion was fast. The biomass components cellulose, hemicelluloses and lignin could be used.

Combustion

Combustion was a process used to convert the chemical energy stored in biomass by burning biomass in air to provide heat, mechanical power, or electricity, etc (Bridgwater, 2003). Fuel briquettes of organic waste materials in compressed form were used as a development intervention to substitute firewood, charcoal or solid fuels. At certain circumstances fuel briquettes could save time, money and reduce deforestation rates also provided income generating opportunity (Boston and Kristen, 2011). In the briquettes making process the addition of binding material improves cohesive force between the seed cake particle resulted in better of compaction with low pressure compaction system (Jongh and Eric, 2010).

Nugroho et al. (2010), Boston and Kristen (2011), and Janske van Eijck (2010) carried out combustion studies with Jatropha seed cake briquettes to determine their feasibility. Boston and Kristen (2011) made briquettes from jatropha cake by mixing starch (10% w/w) as a binding material using pressing machine. In his study he prepared a full set up of recepies that comprised jatropha cake with cow dung, corn husks and saw dust and each composition was tested for combustion. The briquettes made by using cow dung and corn husks were not able to sustain a quality burn. Sawdust briquettes burned better than others with sluggish in maintaining continuous flame. The increase in diameter of seed cake briquette resulted in decrease of combustion gas temperature and not influencing in CO emission significantly.

The combustion of fresh seed cake briquettes resulted in lot of smoke emission, Janske van Eijck (2010) suggested turning of the fresh seed cake into charcoal avoiding the drawback of smoke emission during burning and also to increase the energy content as the weight was reduced due to seedcake burning without oxygen. The charcoal briquettes burned more easily and smoke emission also was less. Almost 40% in weight of the seed cake was lost during char coal briquette making.

Pyrolysis

For best reduction pyrolysis was the most suitable technique, to convert them into value added products which could be easier to transport, storage ,handling and utilizing. Based on the reactor configuration and operating conditions such as temperature, particle size and rate of heating, the key products from biomass pyrolysis could be liquid oil, charcoal, and gases in different composition (Wunderlich, 1990). The technique of slow pyrolysis produced large amount of the solid fuel coke and the fast pyrolysis technique produced bio oils in high yields of up to 80% in weight of dry feed (Huber et al., 2006). The addition of 20% pyrolysis oil maintained the mixtures within the standards of the diesel exception of the viscosity of the mixtures (Monique et al., 2011). Monique et al. (2011), Viboon et al. (2007) and Antony et al. (2010) extracted pyrolysis oil from Jatropha seed cake and pongamia seed cake in an inert atmosphere by supplying heat with different operating condition.

Monique et al. (2011) conducted low temperature conversion (LTC) process at a temperature of 380℃ to 420℃ in an inert atmosphere and evaluated their products. Pyrolysis oil, pyrolytic char, gas and aqueous fractions generated were in relative amounts of 19%, 47%, 12% and 22% (w/w) respectively for seed cake. Antony et al. (2010) conducted experiments on Jatropha de oiled cake by using fluidized bed flash pyrolysis to determine the effects of particle size, pyrolysis temperature and nitrogen gas flow rate on the pyrolysis yields. The maximum oil yield of 64.25 wt% including water content was obtained at 500℃ shown in table 6. The calorific value of pyrolysis oil collected was found to be 19.66 MJ/kg shown in Table 7.

Table 6 Yield of pyrolysis component from Jatropha seed cake against temperature (Antony et al., 2010)

S.N.	Pyrolysis temperature (℃)	Oil yield (%)	Gas yield (%)	Char yield (%)
1	350	42.15	43.24	14.61
2	400	48.40	40.00	11.60
3	450	53.30	38.81	7.89
4	500	64.25	31.86	3.89
5	550	57.69	40.60	1.71

Table 7 Comparison of properties of Pyrolysis oil with diesel (Antony et al., 2010)

Properties	Diesel	Pyrolysis oil	Effects
Calorific value (MJ/kg)	42.151	19.66	Effects in engine performance
Conradson carbon residue	0.30	14.90	Affect the engine, deposited in injector
Kinematic viscosity at 40℃ cSt	2.0~4.5	7.4	Effects in pumping, fuel injection
Flash point ℃	80	140	Safety storage. High fire point leading to starting problem
Pour point	2	4	Effects in cold condition
Ash content (%)	0.01~0.1	0.1	Erosion and corrosions
Acidity as mg of KOH/gm	0.20	87.84	Damage to injector, deposits in fuel systems like pump filters etc.

Viboon et al. (2007) carried out fast pyrolysis trials on Jatropha seed cake waste collected from oil extraction mill using thermo gravimetric analysis (TGA) and quartz tube pyrolyzer and the result indicated that a rise in temperature had led to increase gas yields from 12.9% to 30.1% with decreasing liquid and char yields from 23.2% to 13.3% and 63.9% to 56.5%, respectively. High hydrogen concentration in product gas was also achieved at high temperature with reduction of other hydrocarbon gases.

In case of flash pyrolysis experiments on *Pongamia pinnata* oil cake were done by Raja et al. (2011), at pyrolysis temperature 500℃ the maximum oil yield of 54.8 wt % was obtained with nitrogen gas flow rate of 2.0 m^3/h and particle size of 1.0 mm~1.18 mm. For the particle size of 0.3 mm to 0.6 mm the maximum gas yield of 46.0 wt % was obtained with nitrogen flow rate of 1.75 m^3/h at 500℃. The maximum char yield of 14.1 wt % was obtained at 400℃, particle size of 1.18 mm~1.4 mm, at nitrogen gas flow rate of 1.25 m^3/h. The gross calorific value of pyrolysis oil was found to be 37.45 MJ/Kg.

Literature surveys illustrate that pyrolysis oils in pure form were not suitable for use in modern diesel engines. The major factor was its high viscosity, lead carbon deposits in the combustion chamber and exhaust ports. Thermo catalytic cracking and trans-esterification were the techniques used to solve the problem related to high viscosity. A reduction in viscosity reduced engine operation problems to a great extent (Putun et al., 1999). The presence of ash in the oil could cause erosion and corrosion problems (Elisabeth, 2004). The high flash point suggested that the oil could be safely stored at room temperature but it could led to the starting problems of the engine. Flash point was important from safety view point; that temperature should be as high as practical. Pour point was important for cold weather operation. For satisfactory working, the value should be well below freezing point of the oil used. Hence, considering the persistent problem with pyrolysis oil, it was necessary to upgrade the pyrolysis oil into good quality vehicle fuel, but it was not an economically viable option at present due to production cost would be higher than conventional vehicle fuel.

Gasification

Gasification was simple and commercially well proven technology. Gasification processes converted biomass into combustible gases that ideally contain all the energy originally present in the biomass. In practice, gasification could convert 60% to 90% of the energy in the biomass into energy in the gas. Gasification process involved conversion of various feed stocks to clean producer gas which was a mixture of hydrogen (H_2) and carbon monoxide (CO) by thermo chemical process.

The information available about the use of Jatropha seed husks for energy purposes was limited. Analysis of the husks by Singh et al. (2008) and Vyas and Singh (2007) showed that the husks contained 4% ash, 71% volatile matter and 25% fixed carbon. The calorific value of the husks was 16 MJ/ kg. The Jatropha seed husks had been converted to syngas in an open core down draft gasifier. In that study, it was found that the syngas calorific value and concentration of carbon monoxide, along with gasification efficiency increased with the increase in gas flow rate.

Table 8 and Table 9 highlighted the proximate and ultimate analysis of the seed cake. These values were the main data for predicting the gas gross calorific value composition and temperature limits of the gasifier through mass and energy balances.

Table 8 Proximate analysis

S.N.	Seed cake material	Moisture (%)	Volatile matter (%)	Fixed carbon (%)	Ash (%)	Source
1	Jatropha	8.71	70.92	16.06	4.30	Antony et al., 2010
2	Pongamia	8.12	70.00	17.48	4.40	Raja et al., 2011

Table 9 Carbon, hydrogen and nitrogen content of seed cake

S.N.	Seed cake material	C%	H%	N%	C/N	Source
1	Jatropha	48.80	6.20	3.85	12.70	Ram et al., 2006
2	Pongamia	47.80	6.50	5.50	8.70	Ram et al., 2006

The seed cakes had good volatile matter which gave an attractive potential for energy exploitation through gasification. A fuel with high volatile matter content was more reactive, and therefore could be converted more easily into gas while producing less char. The presence of ash in seed cake was low (4.30 w/w %). Hence this low ash would not create any major problems such as slogging during gasification process.

Even though there was not enough information available regarding gasification of seed cake, energy production through gasification via was advisable. The process of synfuels from biomass would lower the energy cost, improve the waste management and reduce harmful emissions. The syngas thus produced could be used to produce electricity via integrated gasification and combined cycle (IGCC) and auto fuels (Petrol, diesel etc.) via Fischer-Tropsch method (Mahajani, 2009). The following salient features also support conversion of seed cake into combustible gas through gasification.

1. Gasification floor area requirement was lowest per unit output of energy in the form of heat/electricity.

2. High turndown ratio comparable to biogas and higher than steam turbine systems.

3. Easy to operate gasifier, Reliable in operation and Maintenance is easy.

Conclusion

From the literature review it was observed that some of the energy conversion route analysis were done on Jatropha and pongamia seed cake. But there was no detailed study on seed cakes for energy recovery through gasification process. Experiments on non edible seed cake using gasification conversion route to analyze its feasibility for effective energy recovery and its utilization for thermal application and power generation becomes indispensable. So it is necessary to look at the parameters in detail to estimate the constructive features of gasification conversion process on seed cake over biogas generation through bio methanation process and energy generation via thermo chemical processes other than gasification process.

Through experiments the effects of air flow rate and moisture content on biomass consumption rate and the composition of the producer gas generated under various operating conditions are to be studied. The biomass gasifier system could also be appraised for its performance in terms of the equivalence ratio, producer gas composition, calorific value of the producer gas, gas production rate, zone temperatures and cold gas efficiency for further application.

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