Tar cracking of rice husk in biomass gasifier: Reactor design and experimentation

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A two-stage fixed-bed biomass gasifier had been constructed with separate chambers for pyrolysis and gasification of biomass for formation of low tar producer gas. Two-stage gasifier has been experimented to study the effect of operating parameters such as temperature and residence of volatiles in the reactor on conversion of tar and formation of producer gas. Kinetic investigation reveals that optimum parameters for primary and secondary products using single reaction model are comparable with the reported literature. Effect of gasifying agents on composition of gas released from reactor has been studied using gas chromatography and further experiments are performed with air as it yield more combustible gases (about 63%) as compared to other gasification medium.

Keywords: Decomposition, Gasification, Gasifying agent, Kinetics, Pyrolysis

The conversion of biomass by gasification into a fuel suitable for electricity generation greatly increases the usefulness of biomass as a renewable resource. Gasification is robust proven technology that can either use low technology system based on fixed bed gasifier, or more sophisticated system based on fluidized bed technology. Gasification is considered as an efficient process that utilises different types of biomass materials. Biomass gasification has a potential to provide clean and sustainable energy in the developed countries using advanced techniques as well as in the developing countries for providing rural electrification. The produced gas can be used in a number of applications. Gasification includes biochemical and thermo-chemical processes, the former involves microorganisms at ambient temperature under anaerobic conditions, while the latter uses air, oxygen or steam at relatively high temperatures[1,2]. In this study, gasification is referred only to the thermo-chemical conversion of biomass into some useful fuels. It is the conversion of biomass into gaseous fuel by heating in a gasification medium such as air, oxygen or steam. The process converts the intrinsic chemical energy of the carbon in the biomass into a combustible gas in two stages, pyrolysis and gasification. These two processes have been substantially studied to promote renewable energy utilization and solving partially the environmental issues.

Various types of gasification systems have been developed and some of them are commercialized. Technology of gasification, an extension of pyrolysis, provides effective and economical way to convert the low value and wide range of lingo-cellulosic biomass to a gaseous mixture, called producer gas which comprises of hydrogen, carbon monoxide, methane and carbon dioxide[3]. The composition of product gas varies significantly depending on operating conditions such as temperature, operating pressure, gasifying agent, and also on the type of biomass, moisture content in biomass, etc. Moreover, the quality of product gas is associated with other factors such as type of gasifier, residence time and heating rate which is usually associated with the type of biomass, particle size and temperature[4,5].

Tar formation is the major obstacle during gasification process for the synthesis of producer gas. The obtained tar in pyrolysis process appears black, thick and viscous in nature. Tar condensation occurs in low-temperature zones of the gasifier, leading to blockage and failure of the system. Tar is highly undesirable, as it condenses and creates subsequent plugging of downstream equipment, it forms of tar aerosols and polymerizes into more complex structures. Nevertheless, tar is an inevitable product of the thermal degradation of biomass. It is a complex mixture of condensable poly-aromatic hydrocarbons[6]. Presently, there is no common definition of tar. Milne *et al.*[7] defined tar as "the organics, produced under thermal or partial-oxidation regimes (gasification) of any organic material and are generally assumed to be

largely aromatic". The tar in vapour form changes its phase form gas to liquid unless and until it comes in contact with cooler surface. This property of tar makes the producer gas incompatible for use in gas engines having low tolerance for tar. Thus, it becomes necessary to produce the gases containing low tar value for gas engine application. This can be achieved by proper design of the gasifier and the optimization of operating conditions for minimum tar content in producer gas[8]. A constant carrier gas velocity is required to maintain the residence time of volatiles reasonably inside the reactor[9].

Downdraft gasifiers are more efficient in tar destruction than other biomass gasifier configurations and can use wide range of biomass feedstock that releases large amounts of tar. The other advantages of downdraft gasifiers are its relative simplicity, low investment costs and ease of operation. However, it requires biomass of less than 20% moisture and less tars to be released, although smaller than in other gasifier configurations, may still affect the performance of the gasifier[10]. Therefore, it is desirable to completely eliminate or destruct the low residual tar content in the product gas from this type of gasifier. Removal or destruction of tar released in downdraft gasifier is the objective of this research. Much work has been done to remove the tar, with only moderate success, an overview of which is given by Milne et al.[7].

Downdraft gasifier was originally designed and constructed by Hiteshue and co-workers[11] at the U.S. Bureau of Mines laboratories for examining the hydropyrolysis of coals. The two-stage gasifier, evolved from this work, has a cylindrical tube which serves two purposes, as container and as electrical resistance heater. Boroson et al.[12] used two-chamber, connected in series, tubular reactor to study secondary reactions of coal pyrolysis tars and achieved more than 88% tar conversion with various combinations of temperature of the reactor and residence time of volatiles in the reactor.

Modified design of downdraft gasifier was developed by Pindoria et al.[13-15] and successfully used at laboratory scale to produce tars from Eucalyptus wood in pyrolysis section for subsequent tar cracking in gasification section using catalyst. Mild hydropyrolysis in deeper beds of biomass can be suggested better, as it produces lighter, less oxygenated and more stable tars/oils than liquids produced at atmospheric condition. Higher conversions were observed above 800°C in an inert atmosphere as compared to gasification with H_2, CO_2 and steam-He mixture. Catalytic hydrocracking of generated tar was compared with hydropyrolysis products and tar yields after catalytic hydrocracking observed to be decreased with increasing pressure and temperature of the cracking stage.

Nunes et al.[16-18] at Imperial College, configured a smaller (6 mm i.d. and 20 cm long) reactor to produce larger amounts of tar during pyrolysis and its subsequent destruction. Biomass samples yield 47% tar of initial fuel with hot empty second stage; whereas presence of char in second stage substantially decreased the tar yield to less than 0.1%. Several biomass and waste samples were used during experiments, where the effect of temperature, type of char, carrier gas flow rate and other operating conditions was investigated.

Chen et al.[19] investigated the effects of temperature, presence char bed in gasification stage of the reactor, type of char and air as gasification medium on tar emission. Upto 31% tar yield was obtained using single-stage reactor. Studying the effect of operating conditions of reactor resulted decrease in tar yield with rising temperature and residence time; and with decrease in size of char particle.

Dabai et al.[10] also studied the two-stage fixed-bed downdraft reactor to eliminate the tar content in the product gas. Some modifications to the previous lab-scale configuration of downdraft gasifier were introduced to achieve maximum tar cracking. Same observations regarding presence of char and increase in temperature in second stage was obtained as by other researchers[16-19].

Stages of consecutive improvements in the reactor design for better tar conversion have been summarized by Kandiyoti et. al.[9]. Our previous work[20] using two-stage fixed bed was focused on determining the impact of operating conditions on tar cracking. The work established a significant reduction in tar content at higher temperature and residence time. Residence time study of each gaseous product and optimization of kinetic parameters using single reaction model and distributed activation energy model (DAEM) for both homogeneous, as well as heterogeneous tar cracking using char bed in second stage for maximizing gas products and for tar elimination are planned for future work.

Methodology

Reactor design and developments

The reactor configures two stages (i.d. 44 mm and thickness 4 mm) connected together with a throat section and tar trap at the bottom, shown in Fig. 1. First stage represents the drying and pyrolysis zones of a downdraft gasifier, where maximum tar formation occurs. A low, downward flow of inert (Nitrogen) gas is used to sweep the gaseous volatile products, formed from pyrolysis of rice husk, into the second stage of reactor through throat section. A T-piece is fitted at the top of first stage, which connects
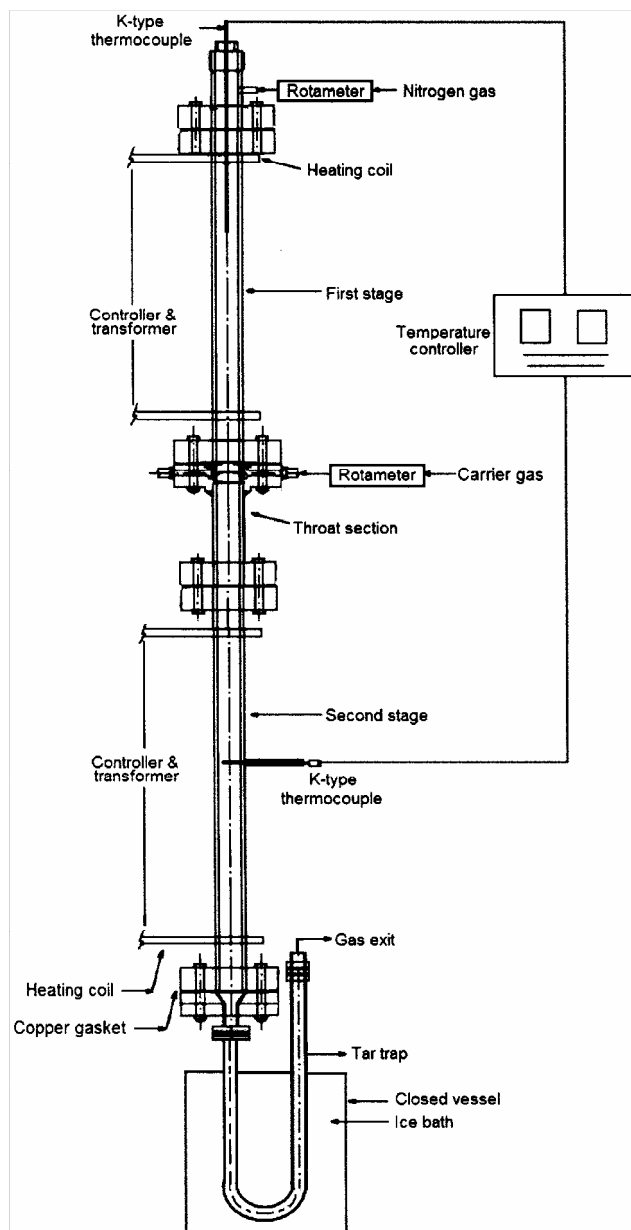

Fig. 1 — Schematic of two-stage biomass gasifier

the gas inlet supply and allows internal reactor temperature measurement with K-type thermocouple.

Second Stage represents the gasification section or tar destruction or high temperature reducing or oxidizing zone, depending on the gasifying agent, immediately below the inert nozzles of throat section. This stage can be used empty (homogeneous) or packed with char or catalyst (heterogeneous) for maximum possible destruction of tar and production of producer gas. It has welded top and bottom flanges. The bottom flange is connected to the tar trap. This stage also has K-type thermocouple for internal reactor for better control of temperature. Both the stages are externally direct resistance heated and the temperatures are controlled separately by means of PID controllers.

Throat section connects both the stages of the reactor. The top flange of throat has been specially designed, having three equally spaced lateral nozzles. This design enables injection of inert gas at the junction of two stages, which in turn allows the control of gas flow in the second stage, independent of the first stage gas flow. The throat comprises of a flange with a removable centre-piece having V-shape[16,17] shown in Fig. 2. The reactor body is insulated to avoid heat radiations in the surrounding. Tar Trap is a simple U-tube fitted with a top flange connected to the outlet of second stage via union. It is immersed in cooling agent, like ice and captures/condenses the volatiles released by biomass sample during gasification. For sampling and venting of product gases, a T-piece is fitted at the outlet of the trap.

Experimental Section

The biomass used in this study was rice husk, received from a local rice mill. Particle size of less than $1000\mu m$ was obtained by grinding and sieving. At 378K for about 6 h, the biomass was dried in oven and stored in air-tight containers for further experimentation.
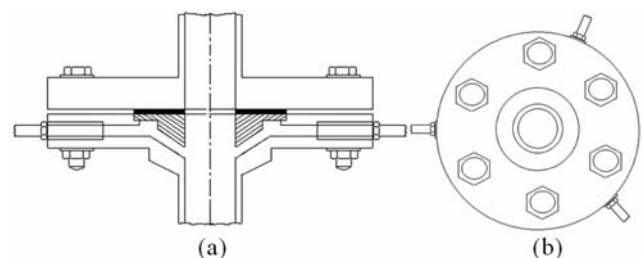

Fig. 2— (a) Front view and (b) Top view of specially designed throated flange

Tar cracking and residence time study had been performed using both the stages with different lengths of the second stage, connected to the downstream of the first stage. Both stages were operated and controlled separately. The operating parameters of first stage are: temperature 773K, heating rate 25 K/min and sample weight 50 g. The first stage was always operated at 773K, as the tar generation takes place mostly in the temperature range of 673-773K; whereas second stage was empty and operated at different temperatures (873 K, 973 K, 1073 K and 1173 K). During operation, a wire mesh plug was inserted from bottom of first stage approximately to a distance of about 50 mm, then after the reactor was loaded with biomass. One more wire mesh was kept between the joint of reactor and tar trap to avoid entrance of char particles in the trap. A 1 LPM flow of inert (nitrogen) gas through a mass flow controller (rotameter) was injected from top of reactor to sweep the gaseous volatiles downwards to the tar trap, dipped in ice bath. Inert gas was also injected at the throat section. The second stage was preheated and maintained at the desired temperature before starting the first stage heating, so as to crack immediately the volatiles released from first stage even at lower temperature.

The present study deliberately started to study the conversion of pyrolysis products of rice husk, and its gasification in the gas containing CO, CH_4 and CO_2 under various operating conditions in two-stage downdraft fixed-bed biomass gasifier. The tars resulting from both configurations (single-stage and two-stage) of the reactor and operating conditions have been characterized by gas chromatography to identify how the yield of residual tar is affected by secondary reactions in the second stage.

Products of gasification

Pyrolysis of rice husk and simultaneous gasification of its vapour phase volatiles gives three products, solid char, liquid tar and gases. Out of these, char and tar yields are measured gravimetrically, whereas gases are analyzed by using gas chromatography. When the reactor cools down to room temperature, char formed in the first stage was taken out and weighed. Fine char particles collected on the wire mesh and recovered from the filtration of tar solution were also weighed and added to total char yield. For collecting tar condensed in tar trap, the trap was washed several times with a mixture of chloroform and methanol (4:1) until clear liquid obtained. The solution was then filtered and collected in sampling flask of the rotary evaporator, to separate the

solvent leaving tar in the flask. Rotary evaporator was operated at 65°C (as boiling point of chloroform and methanol are closed to 65°C) and at 130 rpm. Some authors used to dry the solvent after recovery in an oven, as extra amount of solvent was utilised for washing glassware. But in this study, as no extra solvent was used for washing purpose, the tar was directly weighed when the flask cooled down to room temperature. The yield of char and tar obtained after each experiment was reported in terms of percent initial weight of biomass, on dry basis.

The gases released during each experiment was collected in gas sampling bags and analysed for CH_4, CO and CO_2 using gas chromatography (make: Shimadzu, model: GC-2014). Manual gas sampler (MGS) for gas injection and packed columns (MS-5A and PORAPAK-Q) with thermal conductivity detector were used for gas analysis.

Results and Discussion

Optimization of kinetic parameters

The experiments were performed with an empty heated second stage (homogeneous tar cracking) under the experimental conditions discussed in methodology section. The tar reduction was observed by increasing reactor temperature. It was observed that the empty second stage at elevated temperature reduced the amount of tar from 48.95 to 7.95%. Overall 84% of tar cracking has been observed at longer residence time and higher temperature. Single reaction model was used to correlate the tar cracking and gas production data. Tar cracking studied by Diebold et al.[20] and Liden et al.[21] are compared to the single reaction model results of this study in Fig. 3,
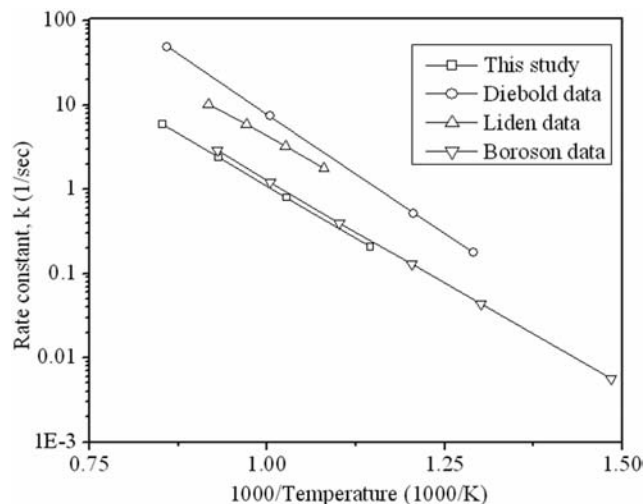

Fig. 3 — Optimum values of kinetic parameters for tar cracking

showing the increasing rate constant with increasing temperature. The best fit kinetic constants are predicted for this data by the technique of two-dimensional surface fitting non-linear regression technique[23]. The optimized kinetic parameters of secondary tar cracking were observed to be comparable with literature[12,20,21] noted in Table 1.

Effect of temperature on primary gaseous yield

The reactor was operated with single stage only and 1LPM flow rate of inert nitrogen was introduced from top of the reactor. The gaseous samples are collected at every 100 K change in temperature and analyzed with gas chromatograph. Respective yields for primary pyrolysis of rice husk are shown in Fig. 4. Primary products were char, which remained in first stage of reactor, the volatiles which are condensed in tar trap and gaseous products.

Effect of gasification medium on secondary gaseous yield

Combinations of inert nitrogen, air and oxygen were tried to analyse the effect on gasification medium of secondary gases. Nitrogen is always injected in the first stage for complete pyrolysis of the biomass, whereas nitrogen, air and oxygen as gasifying medium were injected at throat section. The secondary gases were analyzed using gas chromatography and it was observed that with increase in temperature of second stage, tar cracking

as well as composition of combustible gases (CO and CH_4) increased. At high severity (1073K), about 88% of tar cracking, two-fold increase in methane, 2.5 times increase in carbon monoxide and 1.5 times increase in carbon dioxide were observed. Comparing the representative yield of primary and secondary gases from Table 2, carbon dioxide appears to be both primary and secondary product, as the yield from gasification is about 1.5 times that from primary pyrolysis. Most of carbon monoxide and methane are evolved from secondary reaction as their substantial yield increases during gasification in second stage.

Comparing different gasification medium injected in second stage of reactor, it was concluded that CO_2 forms more due to excess supply of oxygen in second stage, whereas combustible gases (CO and CH_4) yield more in case of air injection in second stage. Other two cases are same for methane formation shown in Fig. 5. H_2 production is less with nitrogen or oxygen as gasifying agents as compared to air, which yield maximum upto 27%. This might occur due to formation of more CO which takes part in water-shift reaction to produce hydrogen. As CO_2 formation should be less and other combustible gases should be more in producer gas, we opted for combination of nitrogen in first stage and air in second stage for further experimentations.

Table 1 — Comparison of kinetic parameters with literature

Earlier research work	A (sec^{-1})	E (kJ/mol)
Boroson et al.[12]	$10^{4.98}$	99.3
Diebold et al.[20]	$10^{5.19}$	87.5
Liden et al.[21]	$10^{6.49}$	108
Our study[22]	$10^{5.08}$	110.00

Table 2 — Comparison of primary and secondary gaseous products

Products	Primary yield (%)	Secondary yield (%)
CO	11.288	26.378
CH_4	5.846	9.704
CO_2	9.789	14.403
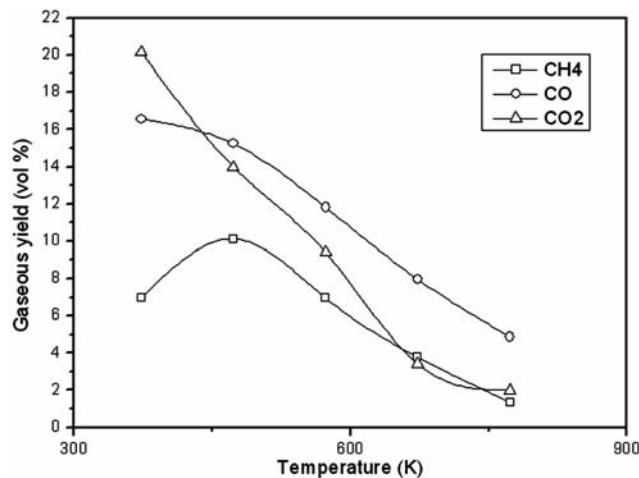
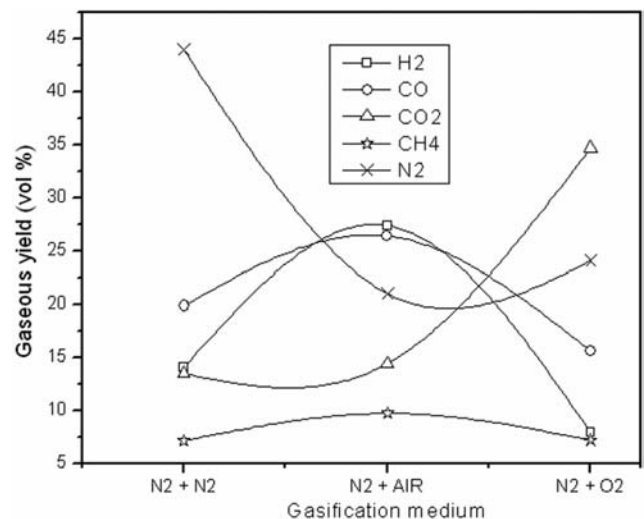Fig. 4 — Primary gaseous composition as function of temperature

Fig. 5 — Effect of gasification medium on secondary gaseous products at 1073 K

Conclusion

We concluded that 88% of the total tar generated in first stage has been cracked at highest severity of the reactor. The common observation was tar yield decreases at higher temperature and longer residence time. Hence, more tar cracking and more gas formation was observed at optimum conditions. Single reaction kinetics for tar cracking approximately agreed with that obtained by Boroson et al.[12], Diebold et al.[22] and Liden et al.[23].

The experimental results of this work identified and quantified major products generated by primary pyrolysis of rice husk and cracking of its tar. Comparing the different gasification medium, air gives better formation of combustible gases H_2, CO and CH_4. Tar cracking as function of temperatures and residence times using air as gasifying agent; and distributed activation energy model for tar cracking as a function of residence time is planned for future work.

Acknowledgement

References

1   McKendry P, *Biores Tech*, 83 (2002) 37.
2   Lan W, Chen G, Ma W, Yan B & Li W, Biomass gasification in China, Proceedings, Power Energy Engineering Conference, (Wuhan Asia-Pacific), 2011.
3   Wang L, Weller CL, Jones DD & Hann MA, *Biomass Bioenergy*, 32 (2008) 573.
4   Bhavanam A & Sastry RC, *Int J Chem Eng Appl*, 2 (2011) 425.
5   Chitti Y & Kemiha M, *Int J Eng Sci*, 2 (2013) 75.
6   Devi L, Ptasinski KJ & Janssen FJJG, *Biomass Bioenergy*, 24 (2003) 125.
7   Milne TA, Evans RJ & Abatzoglou N, Biomass Gasifier Tars: Their Nature, Formation, and Conversion (National Renewable Energy Laboratory, Golden Colorado), 1998.
8   Basu P, Biomass Gasification and Pyrolysis : Practical Design and Theory (Oxford, UK, Elsevier Inc.), Ch 4, 2010.
9   Kandiyoti R, Herod A & Bartle K, Solid Fuels and Heavy Hydrocarbon Liquids: Thermal Characterisation and Analysis (Elsevier, Amsterdam, The Netherlands), First Ed., 2006.
10 Dabai F, Paterson N, Millan M, Funnell P & Kandiyoti R, *Energ Fuel*, 24 (2010) 4560.
11 Hiteshue RW, Friedman S & Madden R, Hydrogasification of High-Volatile A Bituminous Coal (United States Bureau of Mines Report of Investigation No. 6376), 1964.
12 Boroson M L, Howard J B, Longwell J P & Peters WA, *AIChEJ*, 35 (1989) 120.
13 Pindoria R V, Lim J Y, Hawkes J E, Lazaro M J, Harod A A & Kandiyoti R, *Fuel*, 76 (1997) 1013.
14 Pindoria RV, Megaritis A, Messenbock RC, Dugwell R & Kandiyoti R, *Fuel*, 77 (1998) 1247.
15 Pindoria RV, Megaritis A, Herod A A & Kandiyoti R, *Fuel*, 77 (1998) 1715.
16 Nunes S M, Investigation of Tar Destruction Reactions in a Downdraft Gasifier using Biomass and Waste Feedstock, Ph.D. Thesis, University of London, 2007.
17 Nunes SM, Peterson N, Dugwell DR & Kandiyoti R, *Energ Fuel*, 21 (2007) 3028.
18 Nunes SM, Peterson N, Herod AA, Dugwell DR & Kandiyoti R, *Energ Fuel*, 22 (2008) 1955.
19 Chen Y, Luo Y H, Wu W G & Su Y, *Energ Fuel*, 23 (2009) 4659.
20 Khonde RD & Chaurasia AS< Under review in Curr Sci India.
21 Diebold JP, *The cracking kinetics of depolymerised biomass vapors in a continuous tubular reactor*, MS Thesis, Colorado School of Mines, Golden, 1985.
22 Liden AG, A kinetic and heat transfer modelling study of wood pyrolysis in a fluidized bed, MASc Thesis, Ontario, Canada, 1985.
23 Khonde RD & Chaurasia AS, *J Inst Eng India Ser E*, 96 (2015) 23.