Effect of catalysts on combustion of paper mill sludge, paulownia wood and micro algae

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Background

- Combustion is the thermal decomposition of biomass in presence of excess air or oxygen

- Rate determined by monitoring the weight loss versus temperature

- Biomass combustion reaction can be modeled by the rate law (Iyer and Rao, 2002; Maiti et al, 2007)

$$\frac{d\alpha}{dt} = k(1-\alpha)^n$$

$$\alpha = \frac{(W_0 - W)}{(W_0 - W_f)}$$ W_o, W_f are initial and final sample weights

Arrhenius rate equation

'k' can be replaced by Arrhenius parameters, E and A

$$\frac{d\alpha}{dT} = -\frac{dW}{dT} = \frac{A}{\beta} e^{-E/RT} (1-\alpha)^n$$

Assuming n=1

$$\ln\left(\frac{d\alpha}{dT}\right) = \ln\left(\frac{A}{\beta}\right) - \frac{E}{RT} + \ln(1-\alpha)$$

E = Activation energy, which plays significant role in the decomposition reaction,

A = pre-exponential factor, β= heating rate

Previous studies: Catalytic effects on thermal conversion

- Metal catalysts Ni, Pt, Rh, Ru have been commonly used in biomass pyrolyis and gasification (Sutton et al, 2001).

  Demerits: Catalyst poisoning and expensive

- K, Ca and Mg have been reported to catalyze the pyrolysis and gasification (Raveendran et al, 1995)

- Kaolin has been used as a fluid catalytic cracking catalyst

Hypothesis

- Calcium, Kaolin and Char can catalyze the biomass combustion process by reducing the activation energy (E)

Material and Methods

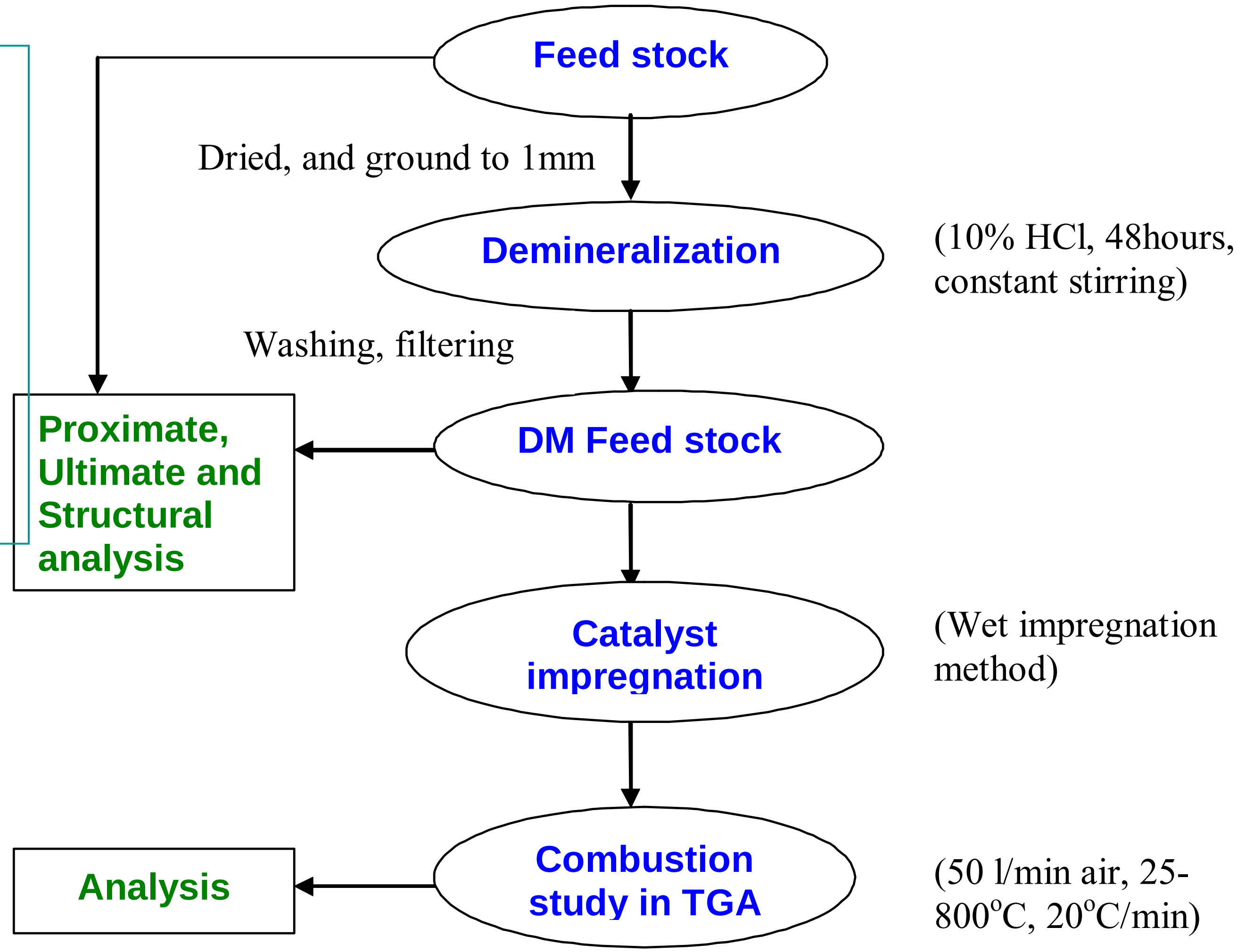
- Feed stocks:
  - Paper mill sludge (PMS)
  - Paulownia wood chips
  - A commercially available micro algae (*C. vulgaris*)

- Catalysts used:
  - Ca ($Ca_3(PO_4)_2$),
  - Kaolin ($Al_2Si_2O_5(OH)_4$),
  - Char (from palm oil shell pyrolyzed at 500°C, 30 min)

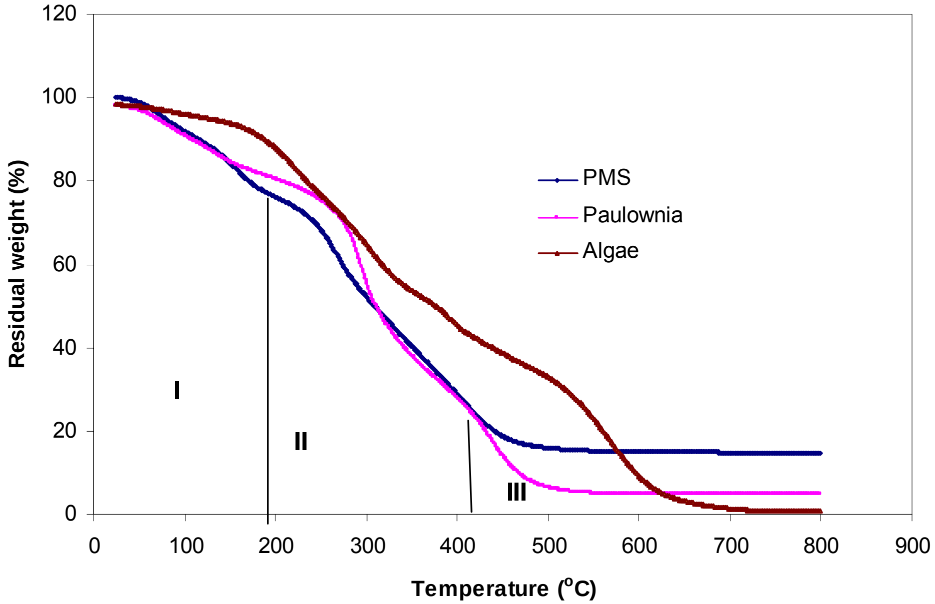
- Inherent minerals of biomass have a substantial effect on its thermal decomposition (Raveendran et al., 1995)

Experimental Methods

➢ <u>Treatments taken in the study</u> : DM feed stock (Control) 3 levels, Catalysts (3 levels) impregnated at 5% & 10% levels of loadings, 18 (total), with 2 replications each 3×3×2 design

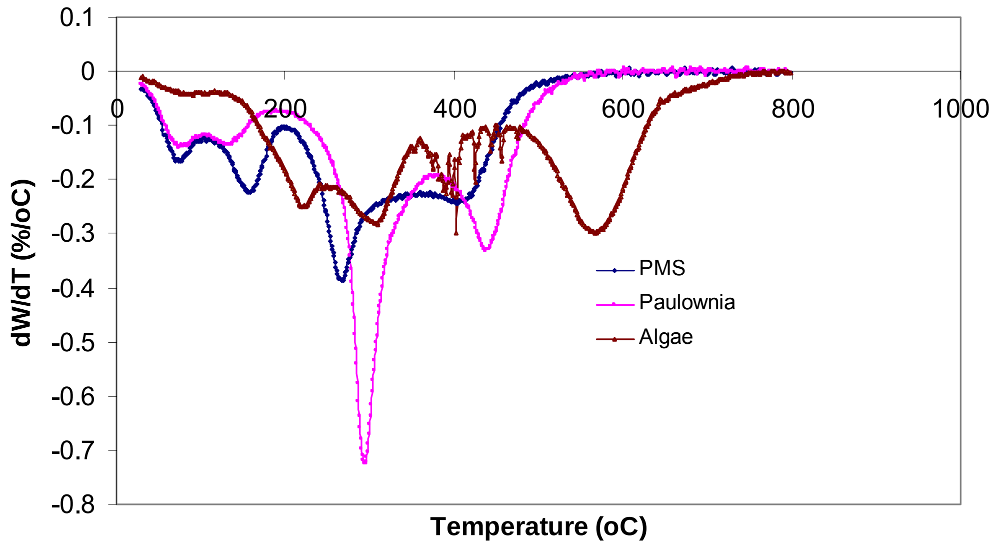


Results and Discussions



TG profile: Two major stages decomposition in PMS and paulownia, but not is the case with algae (multiple stages)

DTG profile: the peaks suggesting major decomposition stages



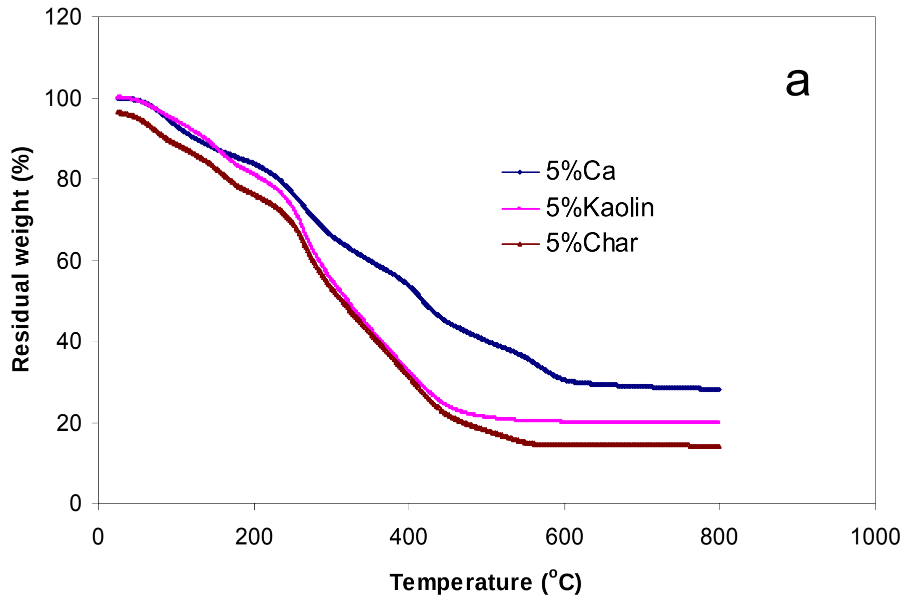
Results and Discussions

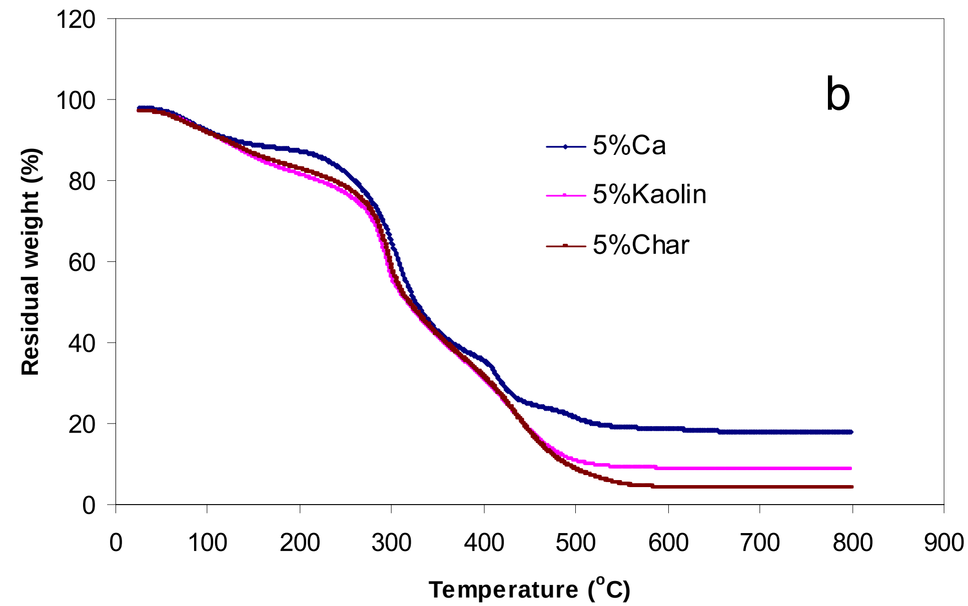
Table 3. Structural composition analysis (%)

Elements	PMS	Paulownia
Cellulose	30.21 ± 2.74	37.02 ± 0.77
Hemicellulose	7.23 ± 2.83	5.79 ± 0.84
Lignin	6.80 ± 0.57	17.49 ± 0.44

Elements	Algae
Protein	59.30
Fat	0.43
Ash	6.76
Carbohydrates	32.03

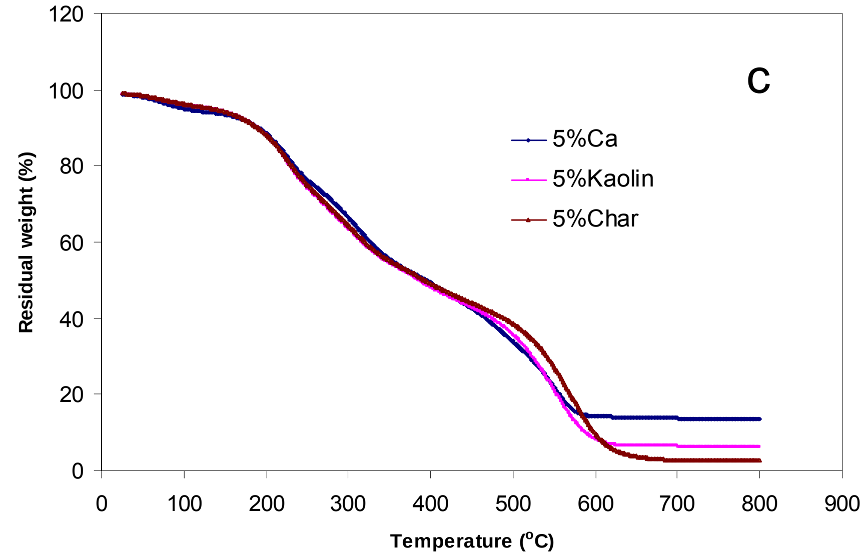
Results and Discussions





TG curve for PMS (a), Paulownia wood (b) and Algae (c) under different catalysts

Algae decomposition was not affected by catalysts



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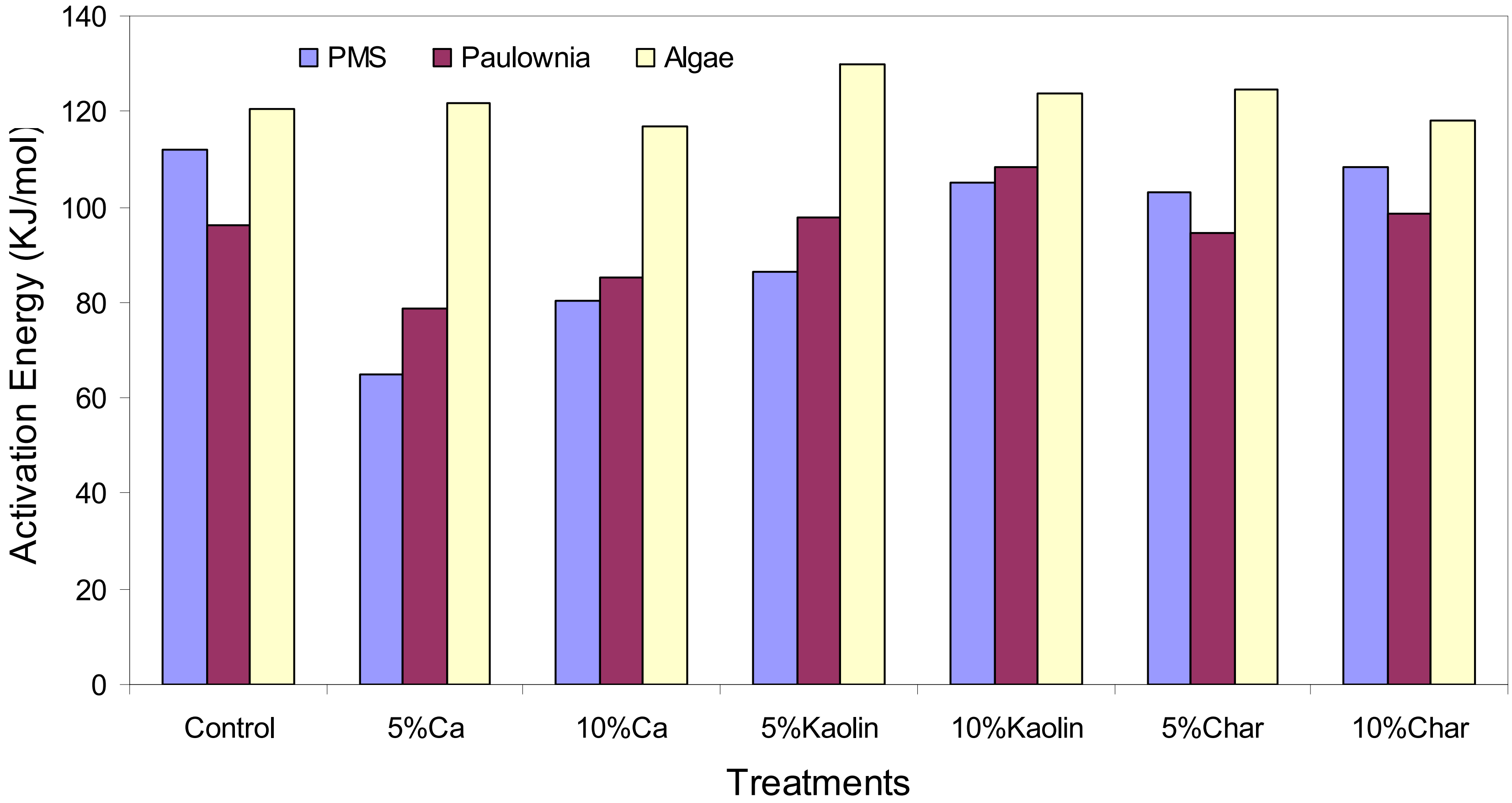

Activation energy (E) was calculated taking the second stage decomposition (as suggested in literatures)

Conclusions

- Among the 3 catalysts taken in the study, Ca was found to have a significantly lower activation energy for the second stage decomposition, for PMS and paulownia wood.

- For algae, decomposition pattern remained unaffected irrespective of catalysts possibly due to protein and lipids (Peng etal.2001)

- There was no significant difference between 5% and 10% loadings on the process in most cases

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Thank you !!!

References

- Fahmi, R., A.V. Bridgewater, L.I. Darvell, J.M. Jones,N. Yates, S. Thain and I.S. Donnison. 2007. The effect of alkali metals on combustion and pyrolysis of Lolium andFestuca grasses, witchgrass and willow. *Fuel 86: 1560—1569.*
- Iyer, P. V. R., T. R. Rao and P. D. Grover. 2002. Biomass: Thermochemical characterization. 3rd ed.1-42, Indian Institute of Technology, Delhi, India.
- Kumar, A., L. Wang, D. A. Yuris, D. A. Jones and M. A. Hanna. 2007. Thermogravimetric characterization of corn stover as gasification/pyrolysis feed stock. *An ASABE Meeting Presentation*, Paper Number 076146, 2007 ASABE Annual International Meeting held during 17-20 June 2007, Minneapolis, Minnesota.
- Guo, J. and A.C. Lua. 2000. Kinetic study on pyrolysis of extracted oil palm fiber: Isothermal and non-isothermal conditions. *Journal of Thermal Analysis and Calorimetry*, 59: 76-774.

References

- Peng, W., Q. Wu and P. Tu, 2001. Pyrolytic characteristics of heterotrophic Chlorella protothecoids for renewable biofuel production. *Journal of Applied Phycology*, 13: 5-12.
- Raveendran, K., A. Ganesh and K. C. Khilar, 1995. Influence of mineral matter on biomass pyrolysis characteristics. *Fuel*, 74 (12), 1812-1822.
- Raveendran, K., A. Ganesh and K. C. Khilar, 1996. Pyrolysis characteristics of biomass and biomass.components *Fuel*, 75 (8), 987-998.
- Stenseng, M., A. Jenses and K. Dam-Johansen, 2001. Investigation of biomass pyrolysis by thermogravimetric analysis and differential scanning calorimetry Journal of Analytical and Applied Pyrolysis, 58, 765-780.
- Suzuki, T., J. Iwasaki, H. Konno and T. Yamada, 1994, Effect of demineralization on the hydrogasification reactivity of iron loaded birch char. *Fuel*, 74(2), 173-178.

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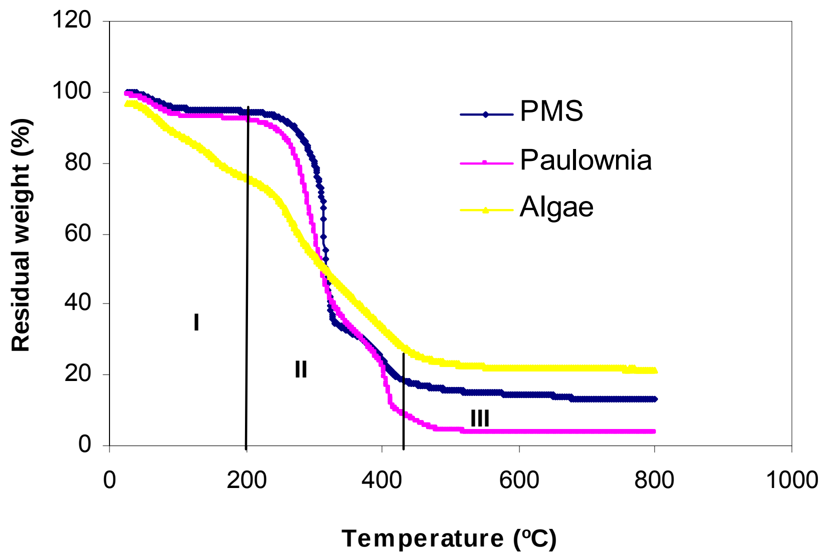

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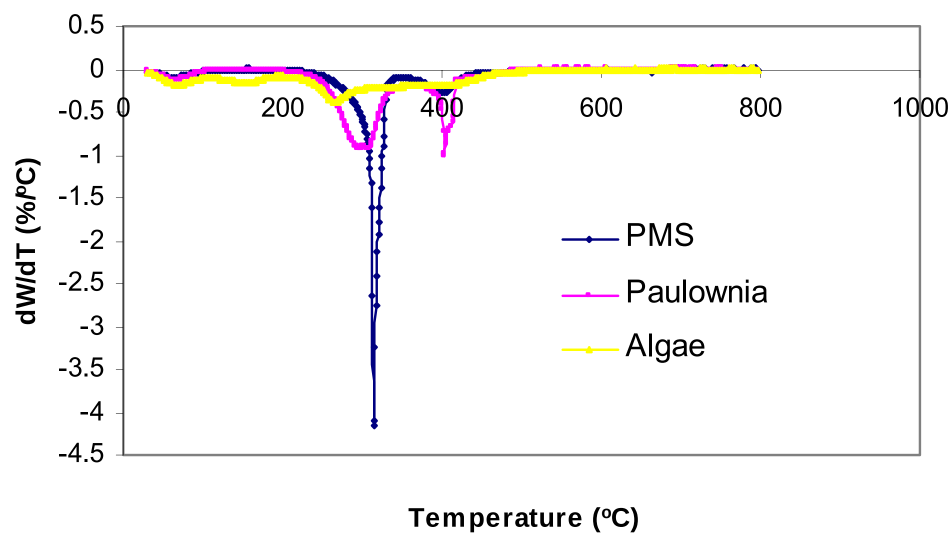

Results and Discussions

Table 1. Proximate analysis (wt% dry)

Elements	PMS	Paulownia wood	Algae
Ash	14.43	3.27	6.76
Volatiles	73.96	79.58	80.82
Fixed Carbon	13.0	19.03	9.54

Table 2. Ultimate analysis (wt% dry)

Elements	PMS	Paulownia wood	Algae
C	40.05	47.41	48.51
H	5.60	6.29	6.95
N	0.80	0.81	9.54
S	0.046	0.08	0.65

**All values are average of 3 replications*

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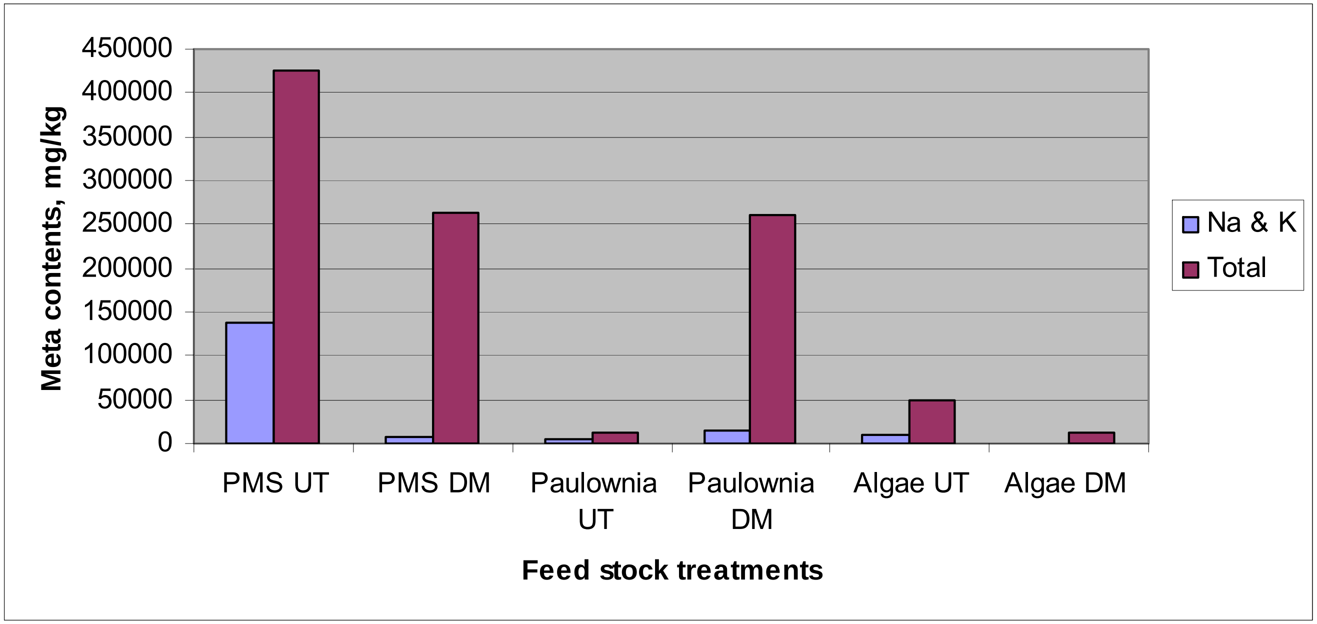

Specific metals and total metals in ash of untreated and demineralized feed stock. Paulownia is showing exception of higher metal content in demineralized treatment than the untreated, it is suspected that labeling of the sample has been altered during sampling

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