IWWATV

Industrial Waste & Wastewater Treatment & Valorisation

THERMOGRAVIMETRIC PYROLYSIS OF WALNUT SHELL AN ASSESSMENT OF KINETIC MODELING

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INTRODUCTION

- With the depletion of fossil fuels and concerns over CO_2 emissions, renewable biomass is now being considered as an important energy resource all over the world.

- Biomass is the third largest primary energy resource in the world after coal and oil.

- Wood and other forms of biomass including energy crops and agricultural forestry wastes are some of the main renewable energy resources available.

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INTRODUCTION

○ The chemistry of biomass is very complicated. But generally it is assumed that biomass has three major carbon containing constituents: cellulose, hemicellulose, and lignin.

Lignin decomposes over a wider temperature range compared to cellulose and hemicellulose, which rapidly degrade over narrower temperature ranges, hence the apparent thermal stability of lignin during pyrolysis.

The rate and extent of decomposition of each of these components depends on the process parameters
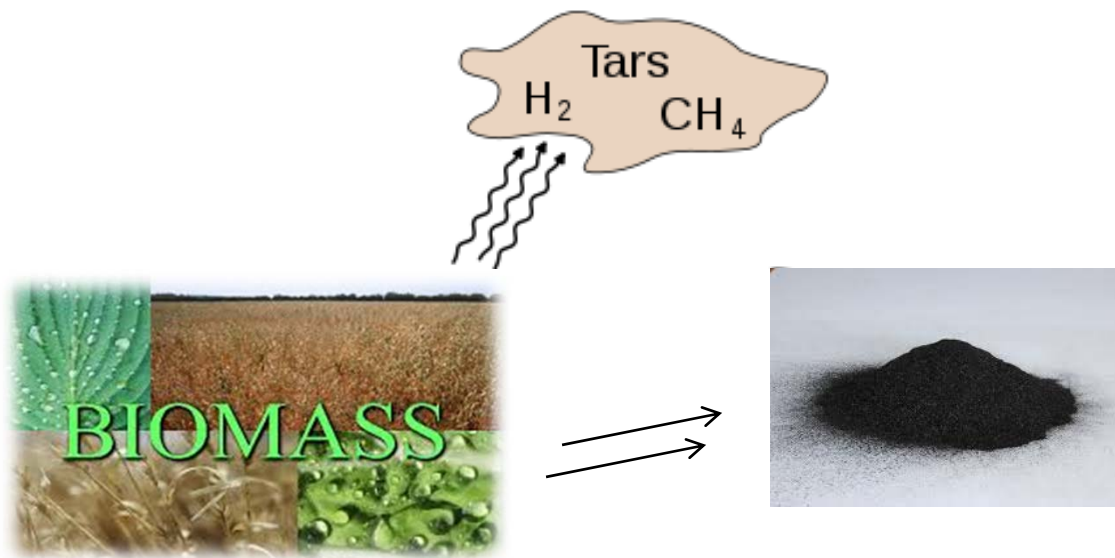
reactor temperature

biomass heating rate

pressure

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PYROLYSIS

- Pyrolysis is a thermochemical decomposition of organic material at increasing temperatures in the absence of oxygen.

- Pyrolysis of biomass has been a major commercial interest with hopes of producing new fuels and intermediate compounds for the chemical industry.

WHY THERMOGRAVIMETRIC ANALYSIS ?

✓ Kinetic analysis of thermal decomposition processes has been the subject interest for many investigators all along the modern history of thermal decomposition.

✓On one side, kinetic data are essential for designing any kind of device, in which the thermal decomposition takes place; on the other side, kinetics is intrinsically related with the decomposition mechanisms.

✓The knowledge of the mechanism allows the postulation of kinetic equations or vice versa, and kinetics is the starting point to postulate mechanisms for the thermal decomposition.

WHY THERMOGRAVIMETRIC ANALYSIS ?

○ Although kinetic studies can be performed in different devices, thermogravimetry (TG) is, by large, the mostly used technique.

○ The advantages of TGA are fast and repeatable data collection of pyrolysis rate, which facilitates a deep investigation of kinetic parameters.

○ In a TG experiment, a modern equipment typically registers hundreds or thousands of experimental points that can be used for kinetic analysis of the reaction. It is clear that the selection of correct model is a critical point in kinetic analysis. Knowing how a model can justify experimental data has been evaluated by many researchers.

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AIM OF <u>THIS</u> STUDY:

- To show the utility of kinetic analysis method based on the complementary use of Coats-Redfern methods,

- To identify the pyrolysis reaction model from non-isothermal TGA data.

- In this work, the TGA study of *walnut shell* was realized using non-isothermal method in order to determine the activation energy and the pyrolysis reaction model.

MATERIALS & EXPERIMENTAL TECHNIQUE

Walnut shell sample has been taken from the Northwest region of Turkey

Dried at room temperature, ground by rotary cutting mill and sieved

Results of proximate and ultimate analysis of WS	Value
Moisture (Wt. %)	8.06
Ash (Wt. %)	0.33
Volatile matter (Wt. %)	76.38
Fixed carbon[a] (Wt. %)	15.23
Holocellulose (Wt. %)	46.13
Oil (Wt. %)	3.29
Lignin (Wt. %)	48.11
Extractives (Wt. %)	3.78
Hemicellulose (Wt. %)	22.18
Cellulose[a] (Wt. %)	23.95
Carbon (Wt. %)	47.50
Hydrogen (Wt. %)	6.39
Nitrogen (Wt. %)	0.46
Sulphur (Wt. %)	-
Oxygen[a] (Wt. %)	47.65
Calorific value (Mj/kg)	16.70

[a] By difference

THEORI...

Coats Redfern Equation by

$$\left[\frac{g(...)}{...}\right]... AR...\left(1-\frac{2...}{...}\right)$$

What is g(α) ?

...t... hand side

...mined from the...

**g(α) represents the integrated form of the conversion dependence, however without specific analytical solution. Several expressions for g(α) have been proposed in the literature as a function of different reaction mechanisms, all of which are based on three concepts: diffusion, nucleation and the order of the reaction.**

n°	Function	Mechanism	g(α)
	Diffusion models		
1	Parabolic law	Diffusion, 1D	α^2
2	Valensi (Barrer)	Diffusion, 2D	$\alpha + (1-\alpha)\ln(1-\alpha)$
3	Ginstling-Broushtein	Diffusion, 3D (column symmetry)	$\left(1-\frac{2\alpha}{3}\right)-(1-\alpha)^{2/3}$
4	Jander	Diffusion, 3D (spherical symmetry)	$\left(1-(1-\alpha)^{1/3}\right)^2$
5	Anti-Jander	Diffusion, 3D	$\left[(1+\alpha)^{1/3}-1\right]^2$
6	Zhrualev, Lesokin and Tempelmen	Diffusion, 3D	$\left[\left(\frac{1}{1-\alpha}\right)^{1/3}-1\right]^2$
	Nucleation models		
7-11	Avrami-Erofeev	n = 1; 1.5; 2; 3; 4	$[-\ln(1-\alpha)]^{1/n}$
12	Power law		α
13	Power law		$\alpha^{1/2}$
14	Power law		$\alpha^{1/3}$
	Reaction order and geometric contraction models		
15	Shrinkage geometry	Column symmetry	$1-(1-\alpha)^{1/2}$
16	Shrinkage geometry	Spherical symmetry	$1-(1-\alpha)^{1/3}$
17-20	Reaction order	n = 0.25; 1.5; 2; 3	$\frac{(1-\alpha)^{1-n}-1}{n-1}$
21	Mampel	n=1	$-\ln(1-\alpha)$

RESULTS AND DISCUSSION

THERMAL DEGRADATION OF WS
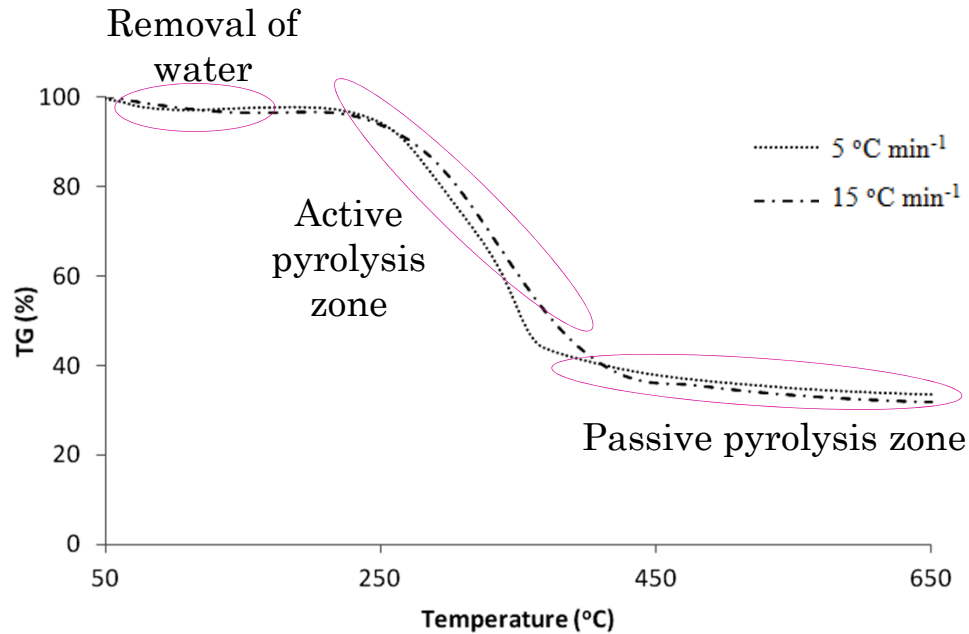
Devolatilization stage plays an important role in the conversion processes. Particularly, attention should be paid to the light hydrocarbons which are producing at the end of thermal degradation. According to TG curves, the mass loss range can be divided into three steps because of variable-slope curves. The first step started at about 50 °C and finished at about 130 °C.

Following the TG curve the main devolatilization step began at about 208 °C and finished at about 372 °C in terms of heating rate and this step indicates decomposition of hemicellulose and cellulose referred as active pyrolysis zone since mass loss rate is high.

After 415 °C passive pyrolysis zone started and mass loss rate was lower at this step. Then, there was no further weight loss essentially. These thermal behaviors clarified by the components of walnut shell. Walnut shell is mainly consisted of hemicellulose, cellulose and lignin like all other lignocellulosic materials.
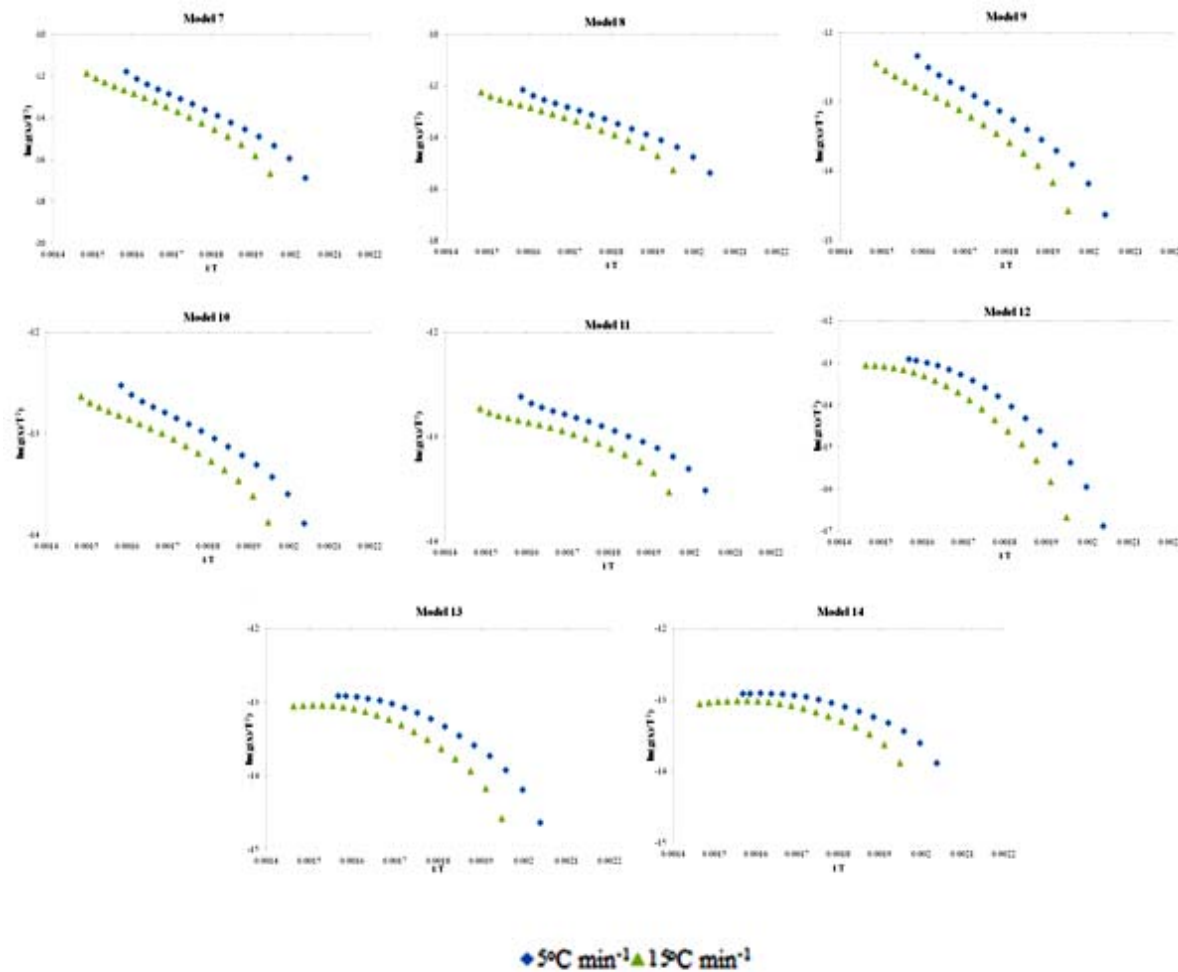
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KINETIC PARAMETERS FOR WALNUT SHELL PYROLYSIS

○ The transformation of the experimental results using the model equations of g(α) was further represented at the heating rate of 5 and 15 °C min^{-1} per mechanism investigated, diffusion, nucleation and reaction order and shrinkage;
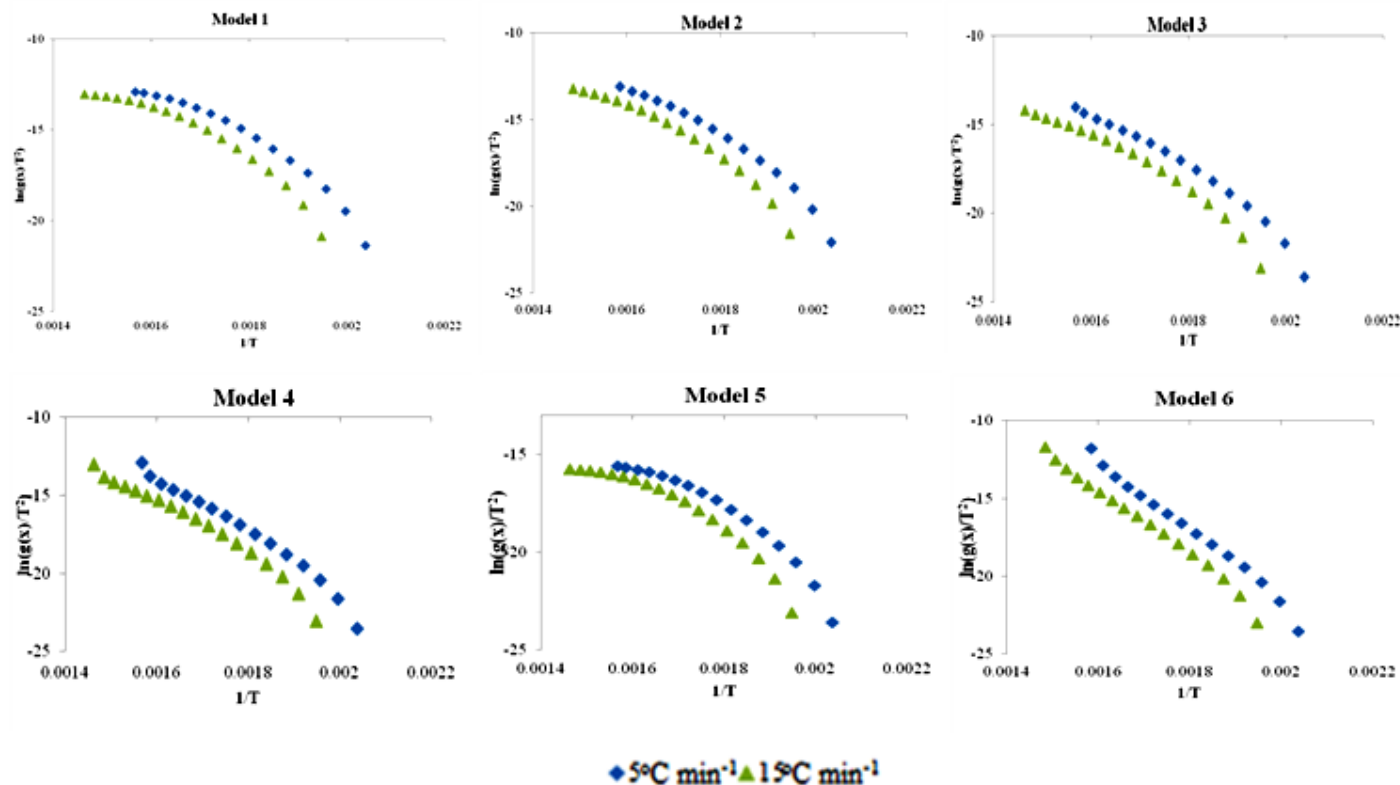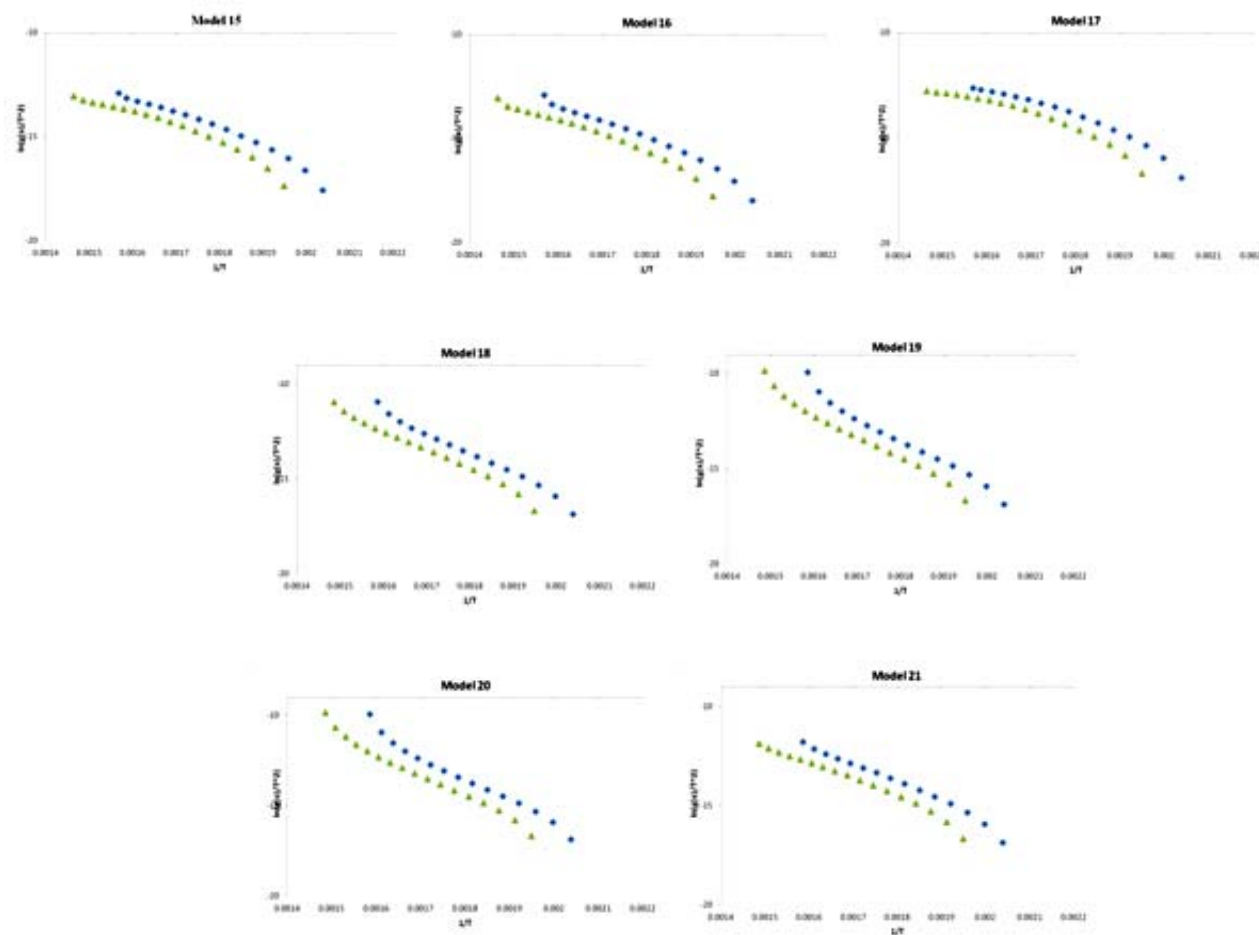

Diffusion models of walnut shell with heating rates of 5 and 15 °C min^{-1}

Nucleation models of walnut shell with heating rates of 5and 15ºC min^{-1}

Reaction order and geometric contraction models of walnut shell with heating rates 5and 15°C min⁻¹

KINETIC PARAMETERS FOR WALNUT SHELL PYROLYSIS

○ A linear fit was observed for both heating values with related to the diffusion approach for mechanism 6.

○ Most often, a linear fit was not obtained for nucleation and geometric contraction models. The activation energy was determined as 192 and 180 kJ min^{-1} for the heating rate of 5 and 15 ^{o}C min^{-1}, respectively.

○ The pre-exponential factor of the Arrhenius equation was calculated as 5.3×10^{8} and 2.1×10^{7} for the heating rate is 5 and 15 ^{o}C min^{-1}, respectively.

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CONCLUSION

- Among pyrolysis of JS three mass loss zones were specified:
  - as removal of water
  - decomposition of hemicelluloses and cellulose
  - decomposition of lignin

- According to the model assessment, the concepts of first order kinetics provide the most suitable design approach.

- For mechanism 6 (3D diffusion model), a linear fit was observed for both heating values. Most often, a linear fit was not obtained for nucleation and geometric contraction models. The isothermal activation energy was determined as 192 and 180 kJ min^{-1} for the heating rate is 5 and 15 ^{o}C min^{-1}, respectively. The pre-exponential factor of the Arrhenius equation was calculated as 5.3×10^8 and 2.1×10^7 for the heating rate is 5 and 15 ^{o}C min^{-1}, respectively.

- Further research will repeat the analyses for pyrolysis of additional biomass, and the same analysis can also be applied to the pyrolysis of plastics.

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THANKS FOR ATTENTION