# Pyrolysis Kinetics of Rice Hull: Influence of Soda Cooking

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*Author's contribution*

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## ABSTRACT

The effect of soda cooking as an effective defibrillation technique of rice hull on its thermal stability has been investigated in this paper. The goal was to investigate the impact of the decomposition of lignin and silica during soda cooking on the thermal stability and kinetics of pyrolysis of the resulting rice hull products by thermal gravimetric analysis (TGA). Soda cooking was carried out using 2.5, 5, 7.5 and 10% NaOH in the cooking liquor at 170°C for 60 minutes. The resulting crude fiber was heated from 25 to 700°C under $N_2$ environment. The results have demonstrated that the removal of silica and lignin from the bulk structure of rice hull by soda cooking affect the thermal stability and pyrolysis kinetics of the rice hull. The final degradation temperature was reduced by 80°C from around 560°C to around 480°C and peaks of maximum decomposition temperatures of the second and third degradation steps shifted to lower temperatures by at least 50°C. The activation energies ranged from 84 to 202 kJ/mol. This revealed increasing trend of pyrolysis energies, from lower to higher decomposition steps. The pyrolysis reaction was a single order reaction since the reaction orders ranged from 0.5 to 0.98. Pyrolysis kinetics can be used to study the effect of chemical treatments of agricultural fibers e.g. by soda cooking.

*Keywords: Activation energy; rice hull; soda cooking; pyrolysis; kinetics.*

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## 1. INTRODUCTION

Rice hull is among the most abundant agro-industrial wastes that have been investigated for various commercial applications, which include among others, the manufacture of cellulosic composites and as source of biomass fuel. One of the main setbacks for the applications of the rice hull has been its high content of amorphous silica on the outer structure [1,2], which is physically and chemically associated with cellulose and lignin in the bulk structure of the rice hull [3]. Thus, silica cannot be removed readily from the structure of the rice hull without affecting the properties of cellulose and lignin due to such structural association.

It is believed that the removal of silica can improve significantly the properties of the rice hull, especially its interaction with various polymeric binders during the manufacture of composites [4]. Also the removal of silica can reduce ash content and thus enhance carbonization. Among the techniques of dissolving silica from the bulk structure of the rice hull include steam explosion [5,6] and soda cooking (pulping). Soda cooking is a thermo-chemical treatment process of lignocellulosic biomass. It involves heating the biomass immersed into a solution NaOH of various concentrations at various temperatures to extract cellulose by dissolving non-cellulosic components including lignin and volatile components. It has been demonstrated that NaOH at high temperature can dissolve significant proportions of both silica and lignin from the bulk structure of the rice hull while retaining substantial amount of crude cellulosic fibers [7].

Pyrolysis provides information on thermo-chemical reactions of a biomass when undergoing decomposition into gaseous, tar and chars products. Determination of the kinetics parameters of a decomposing biomass can help to obtain indirectly information on what takes place during thermo-chemical conversion processes of the biomass, as well as information on its structure and composition [8-10].

This study was initiated to establish the influence of soda cooking of rice hull on its properties by following the kinetics of pyrolysis. The goal was to gain an understanding of the pyrolysis characteristics of the extracted rice hull samples by relating their thermal stability and thermo-chemical reactions to their composition or structure.

It has been demonstrated previously that thermo-chemical reactions of lignocellulosic biomasses during pyrolysis is influenced by the proportions and characteristics of their major constituents, which include cellulose, hemicelluloses and lignin [8,10-12]. With silica being among the most predominant components in the rice hull, its influence on the pyrolysis kinetics cannot be overemphasized given the facts that it is the most heat resistant component that also cannot be dissolved readily from the rice hull without affecting cellulose and lignin [3,7]. Therefore, pyrolysis can be used to aid an understanding of the influence of soda cooking on the composition or structure of the extracted rice hull.

Several methods have been proposed for describing global pyrolysis kinetics of rice hull and other biomasses using thermogravimetric analysis (TGA) based on single or multi-step reactions [12,13]. These methods can be categorized from the Arrhenius equation (Equation 1); into the differential equation methods proposed by Freeman and Carroll [14], Friedman [15] and many others and the integral methods developed by Coats and Redfern [16], Ozawa [17], Zsako [18] and others.

$$\frac{d\alpha_i}{dt} = A_i \exp\left(\frac{-E_i}{RT_i}\right)[1 - \alpha_i]^{n_i} \tag{1}$$

For decomposition steps $i = 1, 2, \ldots m$

where: $\alpha_i = \left(w_{o_i} - w_i / w_o - w_f\right)$ is the fraction of decomposed biomass at any temperature $T_i$ at step *i*, *w* is mass of the sample at any instant t. $w_o$ is the initial mass, $w_f$ mass at the end of the reaction step, and *E* is the activation energy.

Equation (1) can be consolidated to give Equation (2) for a dynamic decomposition process at the heating rate $\beta$;

$$\ln\left(\frac{d\alpha_i}{dT}\right) = \ln\left(\frac{A_i}{\beta}\right) + \frac{-E_i}{RT} + n_i \ln(1 - \alpha_i) \tag{2}$$

The limitations of most of the integral methods include their inability to determine all the three kinetics parameters (*E, n* and *A*) simultaneously without requiring prior knowledge of at least one of them, particularly the reaction order, n [19]. It has been demonstrated [19] that the differential method proposed by Freeman and Carroll can predict all the kinetics parameters with reasonable accuracy from the slopes of the

regression lines if Equation (2) can be manipulated into Equations (3) to (5).

$$\frac{\Delta[\ln(d\alpha_i/dT)]}{\Delta[\ln(1-\alpha_i)]} = -E_i \frac{1}{R\Delta[\ln(1-\alpha_i)]}\Delta\left(\frac{1}{T}\right)+n_i \quad (3)$$

The slope of $\frac{\Delta\ln(d\alpha/dt)}{\Delta\ln(1-\alpha)}$ versus $\frac{\Delta(1/T)}{\Delta\ln(1-\alpha)}$ plot can be used to obtain the activation energy E.

The reaction order (*n*) and the pre-exponential factor (*A*) can be determined from Eqs (4) and (5), respectively. Eq (5) was obtained by subtracting Eq (2) at two different temperatures.

$$\frac{\Delta\ln(1-\alpha_i)}{\Delta\ln(d\alpha_i/dT)} = \frac{E_i}{n_i}\frac{\Delta(1/T)}{R\Delta\ln(d\alpha_i/dT)}+\frac{1}{n_i} \quad (4)$$

$$\frac{\Delta[\ln(d\alpha_i/dT)/\ln(1-\alpha_i)]}{\Delta[1/(T\ln(1-\alpha_i))]} =$$
$$\ln\left(\frac{A_i}{\beta}\right)\frac{\Delta(1/\ln(1-\alpha_i))}{\Delta[1/(T\ln(1-\alpha_i))]} - \frac{E_i}{R} \quad (5)$$

The regression equations (Equations (3) to (5)) developed by Lin and Fan [19] from the Freeman and Caroll method were therefore applied in this paper to supplement the previous study [7] on the influence of soda cooking of rice hull at 170°C for 60 minutes using 2.5, 5, 7.5 and 10% of NaOH on the properties of the rice hull, using pyrolysis kinetics. The intervals of the regression equations were selected from the degradation steps to obtain the parameters that predict reasonably the pyrolysis kinetics of the tested rice hull samples.

## 2. MATERIALS AND METHODS

### 2.1 Original Material

The original material for the pyrolysis reaction was rice hull, an agro-industrial waste obtained from rice mills (Tanzania).

### 2.2 Soda Cooking

About 100 grams of rice hull were charged into the autoclaves containing 2.5, 5, 7.5, and 10% of NaOH in the cooking liquor. The autoclaves were heated in ethylene glycol bath at 170°C for 60 minutes. The ratio of total liquids to total solids in the cooking liquor was maintained at $4\,\text{litres/kg}$.

The digested rice hull was thoroughly rinsed with deionized water to stop further reaction and was finally vacuum-filtered to extract the fibrous rice hull, which was then dried at ambient temperature for 2 days. The composition of the rice hull samples used in this experiment has been reported previously [7].

### 2.3 Pyrolysis Kinetics

TGA was performed to characterize the pyrolysis kinetics of untreated and soda cooked rice hull using Mettler Toledo TGA/SDTA851 system. The test was conducted between 25°C and 700°C at 10°C/min in inert atmospheres of $N_2$ at a flow rate of 50 ml/min. The test samples were homogenized by crushing prior to weighing to 12.0±0.5 mg and subsequent charging into the TGA furnace.

## 3. RESULTS AND DISCUSSION

### 3.1 Influence of Soda Cooking on Pyrolysis

The TGA curves showing pyrolysis decomposition patterns of the rice hull samples are indicated in Fig. 1. By excluding the preliminary steps, which involved the removal of light volatile substances such as moisture and hemicellulose between 67 and 200°C, it can be shown that all the samples decomposed in two main steps (200-400°C and around 400-500°C) before the plateaus. These steps represent the decomposition of cellulose and lignin and subsequent carbonization of these components into tar and volatile products followed by the degradation of silica. The overlaps observed between the decomposition steps especially for the untreated rice hull and the soda cooked rice hull samples with 2.5 and 5% NaOH explain a broad range of carbonization and competing reactions of the decomposing cellulose and lignin components. The results have revealed further that lignin, which has a broad range of decomposition overlapping from 300 to over 450°C [8,11] was retained in almost all the samples at varying proportions. It demonstrates further that there was no substantial removal of lignin from the rice hull especially at lower concentrations of 2.5 and 5% NaOH. This could be associated with complex structural and chemical association of cellulose, lignin and silica in the bulk structure of the rice hull [3,7].

It can be seen further in Fig. 1 and more explicitly in Table 1 that the final temperature of the last step of pyrolysis for rice hulls treated with at least 7.5% NaOH was reduced from around 560°C to

around 480°C. This may be related to the reduction in thermal stability of the rice hull samples after the removal of significant proportions of the most heat resistant components of rice hull, which are silica and lignin during soda cooking [7]. The interval between 300 and 500 has been ascribed to partial depolymerization of cellulose and subsequent decomposition of cellulose and lignin [8]. An intermediate step between 400 and 500°C was also noted for the rice hull samples prepared from 7.5 and 10% NaOH. This step represents the termination of cellulose decomposition at around 400°C and the start of the decomposition of retained lignin between 400 and 450°C. Above this step, there is no further decomposition suggesting that all the cellulose and the remaining lignin were completely carbonized at 450°C; leaving out silica and the carbonized residual products.

Previous studies have described global pyrolysis of biomass into four main stages [20]. The first stage involves the evolution of moisture below 220°C, which is followed by decomposition of hemicellulose between 220-315°C and cellulose in the range of 315-400°C. The first stage of pyrolysis has been attributed to structural relaxation of biomass while the subsequent stages have been described to be complex [20] probably due to overlapping and competing decompositions of several products. Although the decomposition of lignin has been described to be the final stage, it has a wide range of decomposition temperature overlapping the hemicellulose and cellulose stages [20] as also indicated above in this study.

The derivative TGA curves in Fig. 2 show that maximum decomposition of all samples occurred in the second peak. The results show further the overlaps between the second and third decomposition steps of untreated rice hull and the soda cooked rice hull with less than 7.5% NaOH. The maximum decomposition peaks of the third steps occurred at higher temperatures in these samples compared to the samples, which were prepared with the cooking liquor containing at least 7.5% NaOH. This demonstrates a remarkable influence of lignin and silica contents on the thermal stability of the rice hull samples. Removal of a considerable proportion of lignin and silica during soda cooking, leaving mainly cellulose, reduced slightly the thermal stability of the rice hull as demonstrated by shifting of the peak temperatures of the second and third steps to lower temperatures by at least 50°C. Overlaps

between the second and third peaks of the untreated and the rice hull treated with lower concentrations of NaOH shown in Fig. 2 is attributed to the presence of retained lignin in the samples as described earlier. The association of the three major components of the rice hull and the competing pyrolysis reactions to volatiles and char in this stage may have influenced significantly the decomposition of the rice hull leading to the overlap as suggested by Sonobe et al. [20]. According to them [20], this stage is the most distinctive pyrolysis stage of lignocellulosic materials, which has a strong dependence on the composition and structure of the biomass. The results in Figs. 1 and 2 attest this by confirming that soda cooking affected the composition and structure of the rice hull.

A kneel on the first stage of the untreated rice hull curve between 200 and 310°C corresponds to the decomposition of hemicelluloses, which occurs around 220 and 315°C [9-11]. This peak is absent in all soda cooked rice hull samples suggesting that the hemicelluloses was readily hydrolyzed by the alkaline cooking liquor.

## 3.2 Influence of Soda Cooking on Pyrolysis Kinetic

Table 2 shows the kinetics parameters of various rice hull samples after pyrolysis. As it can be shown in the table, maximum decomposition occurred in the second step whereby at the maximum peak temperatures about 60% of the sample had already decomposed. The activation energy ranged from 84 to 202 kJ/mol and is generally observed to have an increasing trend from lower to higher decomposition steps. The reaction order is between 0.5 and 0.98. This has also been represented graphically in the Appendix A in Figs. A1 to A5. These results do not show any consistent trend with the degradation or with NaOH treatment. The reaction orders obtained are close to 1, which suggest that the pyrolysis reaction involved was a single order reaction. On the other hand, the pre-exponential constant A seemed to increase for the rice hull samples treated with higher NaOH dosage. The inconsistence revealed in the values of A may be associated with multiple reactions that were involved during the pyrolysis process.

From the results obtained, it is difficult to quantify the kinetics parameters of the major rice hull components (cellulose and lignin) due to competing and overlapping reactions that took

place as discussed previously. However, as for the samples treated with higher NaOH dose, especially the 10% sample and the fact that part of lignin and most of silica was removed from this sample during soda cooking, it can be inferred that the kinetics parameters presented for the 7.5% and mostly the 10% sample represents the global kinetics of cellulose and retained lignin. Previous studies [8] show the activation of the three cellulosic components. The activation energy for cellulose is 150 - 250 kJ/mol,

hemicellulose is 100 - 300 kJ/mol, and lignin is 100 - 230 kJ/mol. Sonobe and co-worker [20] also investigated the pyrolysis of agricultural residues and reported similar range of the activation energies for rice straw (170 kJ/mol), rice husk (174 kJ/mol) and cellulose (185 kJ/mol). They fall within the ranges of the activation energies of 113 and 202 kJ/mol obtained for the pyrolyzed rice hull samples in this paper.

**Table 1. Main pyrolysis steps of rice hull**

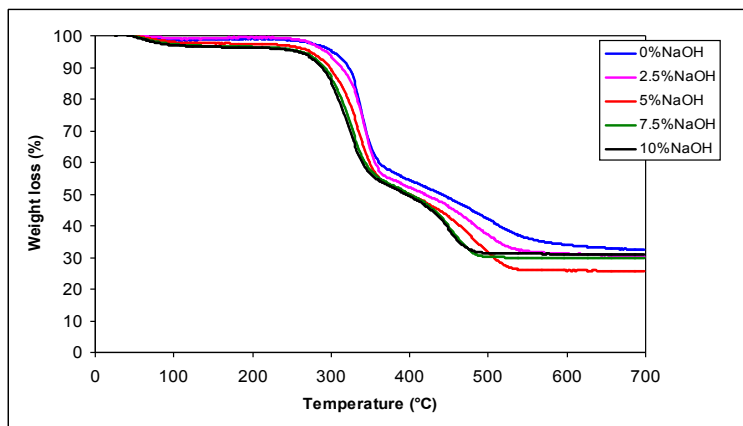| (% NaOH) | Main decomposition step 1 | | Main decomposition step 2 | |
|---|---|---|---|---|
| | Onset temp (°C) | End-set temp (°C) | Onset temp (°C) | End-set temp (°C) |
| Untreated | 280 | 364 | 364 | 569 |
| 2.5 | 269 | 359 | 359 | 547 |
| 5.0 | 259 | 352 | 352 | 539 |
| 7.5 | 259 | 347 | 347 | 487 |
| 10.0 | 259 | 347 | 347 | 478 |



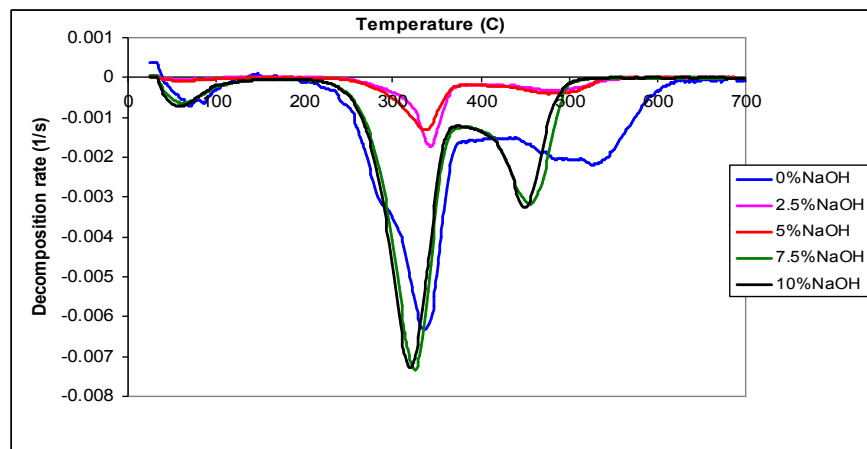**Fig. 1. Decomposition mechanisms of various rice hull products during pyrolysis**



**Fig. 2. Peak temperatures of rice hull products during pyrolysis ob the DTG curve**

**Table 2. Kinetics parameters of thermal degradations of rice hull**

| Liquor Conc. (%NaOH) | Mass loss step (°C) | Step $T_{max}$ (°C) | Mass loss (%) up to $T_{max}$ | Regression step (°C) | Activation energy (kJ/mol) | Reaction order, n | Freq. factor, A (min-1) |
|---|---|---|---|---|---|---|---|
| Untreated | 280-310 | 285 | 3.35 | 248-289 | 174.4 | 1.73 | $2.59 \times 10^{-3}$ |
| | 310-364 | 340 | 9.36 | 331-362 | 209.5 | 0.45 | $4.76 \times 10^{-3}$ |
| | 364-569 | 400 | 62.12 | 373-389 | 59.3 | 0.03 | $2.16 \times 10^{-3}$ |
| 2.5 | 236-352 | 343 | 27.50 | 256-359 | 111.8 | 0.54 | $1.63 \times 10^{6}$ |
| | 352-547 | 491 | 62.53 | 439-521 | - | - | - |
| 5.0 | 259-356 | 339 | 23.32 | 248-353 | 116.3 | 0.59 | $3.62 \times 10^{5}$ |
| | 356-540 | 485 | 67.92 | 433-524 | 84.7 | 0.78 | $2.44 \times 10^{4}$ |
| 7.5 | 241-377 | 328 | 23.82 | 250-357 | 119.1 | 0.84 | $2.29 \times 10^{8}$ |
| | 390-511 | 455 | 62.02 | 418-485 | 133.4 | 0.73 | $1.46 \times 10^{8}$ |
| 10.0 | 259-347 | 322 | 27.68 | 242-349 | 113.8 | 0.91 | $4.85 \times 10^{8}$ |
| | 347-478 | 452 | 59.07 | 436-469 | 202.2 | 0.98 | $7.89 \times 10^{13}$ |

## 4. CONCLUSION

The removal of silica and lignin in rice hull apparently affected the thermal stability and pyrolysis kinetics of the rice hull. The final degradation temperature was reduced by 80ºC from around 560ºC to around 480°C and the peaks of maximum decomposition temperatures of the second and third steps shifted slightly to lower temperatures by at least 50ºC. This was first attributed to the removal of lignin which decomposes in the same temperature range. Secondly, the removal of silica, which is the most heat resistant component in rice hull that is structurally associated with both cellulose and lignin also significantly reduce the thermal stability. The overlaps between the second and third decomposition steps of the untreated and the rice hull samples soda cooked with 2.5 and 5% NaOH not only explain a broad range of carbonization and competing reactions of lignin and cellulose but also the presence of silica to influence the decomposition of lignin and cellulose due to their structural association. The association of these three components and their associated competing pyrolysis reactions to volatiles and char products influenced significantly the decomposition of the rice hull leading to the observed overlap.

The activation energy ranged from 84 to 202 kJ/mol and generally revealed an increasing trend from lower to higher decomposition steps. The pyrolysis reaction was a single order reaction since the reaction orders ranged from 0.5 to 0.98.

## COMPETING INTERESTS

Author has declared that no competing interests exist.

## REFERENCES

1. Chandrasekhar S, Satyanarayana KG, Pramada PN, Raghavan P, Gupta TN. Review processing, properties and applications of reactive silica from rice husk—an overview. Journal of Materials Science. 2003;38(15):3159-3168.
2. Houston DF, Rice Hulls. In rice chemistry and technology. (Ed. DF Houston). St. Paul, MN, American Association of Cereal Chemists. 1972;301-352.
3. Park BD, Wi SG, Lee KH, Singh AP, Yoon TH, Kim YS. Characterization of silica distribution in rice husk using microscopic and micro-analytical techniques. Biomass and Bioenergy. 2003;25:19-27.
4. Ndazi BS, Karlsson S, Tesha JV, Nyahumwa CW. Chemical and physical modifications of rice husks for use as composite panels. Composites Part A. 2007; 38:925-935.
5. Gerardi V, Minelli F, Viggiano D. Steam treated rice industry residue as an alternative feedstock for wood-based particleboards industry in Italy. Biomass and Bioenergy. 1998;14(3):295-299.
6. Ndazi BS, Karlsson S. Characterization of the potential of soda cooking to extract fibrous residues from rice hulls. Polymers from Renewable Resources. 2010;1(3):143-159.
7. Caballero JA, Font R, Marcilla A, Cones JA. New Kinetics Model for thermal decomposition of heterogeneous materials. Industrial and Engineering Chemistry Research. 1995;34:806-812.
8. Caballero JA, Conesa JA, Font RM. Pyrolysis kinetics of almond shell and olive stones considering their organic fraction.

Journal of Analytical and Applied Pyrolysis. 1997;42:159-175.

9. Conesa JA, Domene A. Biomass Pyrolysis and Combustion Kinetics through n-th Order Parallel Reactions. Thermocimica Acta. 2011;523(1):176-181.

10. Yang H, Yan R, Chen H, Zheng C, Lee DH, Liang DT. In-depth investigation of biomass pyrolysis based on three major components: Hemicellulose, cellulose and lignin. Energy and Fuels. 2006;88:1781-1788.

11. Liu N, Fan W, Dobashi R, Qizhao L. New mass loss kinetics model for thermal decomposition of biomass. Chinese Science Bulletin. 2001;46(16):1398-1402.

12. Yin CY, Goh BM. Thermal degradation of rice husks in air and nitrogen: Thermogravimetric and kinetic analyses. Energy Sources, Part A: Recovery, Utilization, and Environmental Effects. 2011;34(3):246-252.

13. Freeman ES, Carroll B. The application of thermoanalytical techniques to reaction kinetics: The Thermogravimetric Evaluation of the Kinetics of the Decomposition of Calcium Oxalate Monohydrate. Journal of Physical Chemistry. 1958;62:394-397.

14. Friedman HL. Kinetic of thermal degradation of char-forming plastics from thermogravometry. Application to a phenolic resin. Journal of Polymer Science Part C. 1964;6:183-195.

15. Coats AW, Redfern JP. Kinetic parameters from thermogravimetric data. Nature. 1964;201:68-69. DOI:10.1038/201068a0.

16. Ozawa T. A new method of analyzing thermogravimetric data. Bulletin of Chemical Society of Japan. 1965;38(11):1881-1886.

17. Zsako J. Kinetic analysis of thermogravimetric data. Journal of Physical Chemistry. 1968; 72:2406-2411.

18. Lin NA, Fan WC. Critical consideration on the freeman and carroll method for evaluating global mass loss kinetics of polymer thermal degradation. Thermochimica Acta. 1999;338:85-94.

19. Sae-Ueng U, Sritrakul N, Soponpongpiapa N. Kinetics of biomass decomposition in pyrolysis and torrefaction process. J Sci Technol MSU. 2013;32(1):64-71

20. Sonobe T, Pipatmanomai S, Worasuwannarak N. Pyrolysis Characteristics of Thai-agricultural Residues of rice straw, rice husk, and corncob by TG-MS technique and kinetic analysis. *In* Proceedings the 2nd Joint International Conference on Sustainable Energy and Environment (SEE 2006) C-044 (P) 21st to 23rd November 2006, Bangkok, Thailand; 2006

## APPENDIX



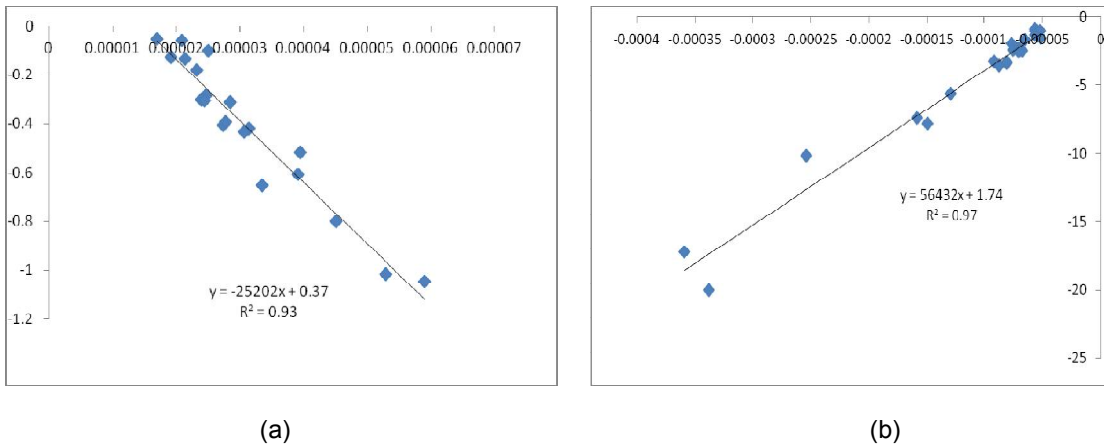(a)                                          (b)

**Fig. A1. Sample regression curves for determination of (a) activation energy (b) reaction order of untreated rice hull**



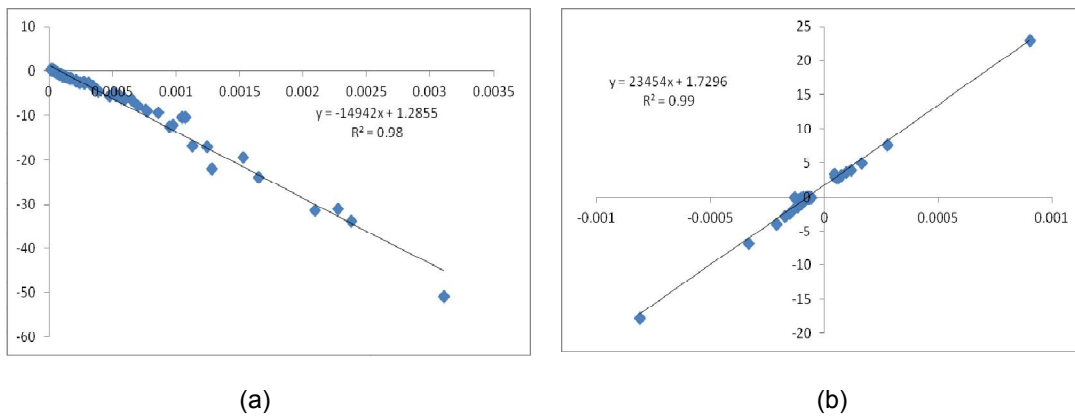(a)                                          (b)

**Fig. A2. Sample regression curves for determination of (a) activation energy (b) reaction order of 2.5% NaOH cooked rice hull**
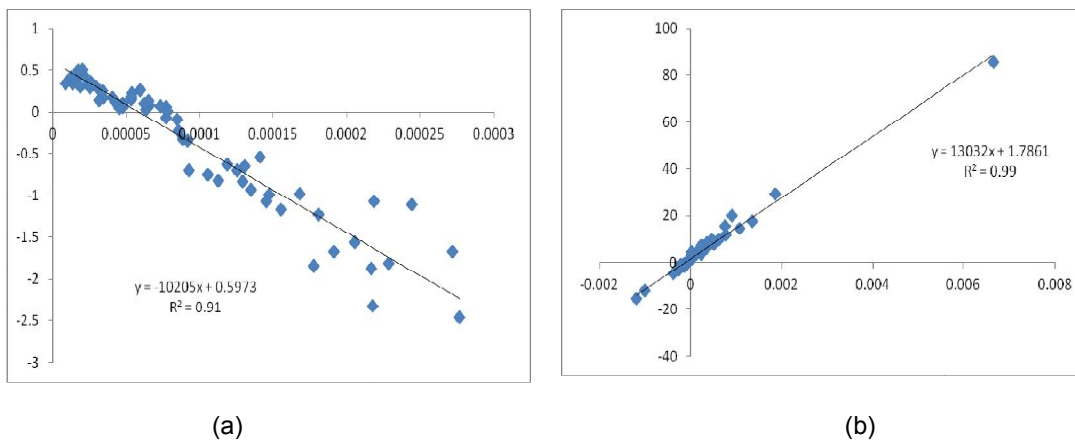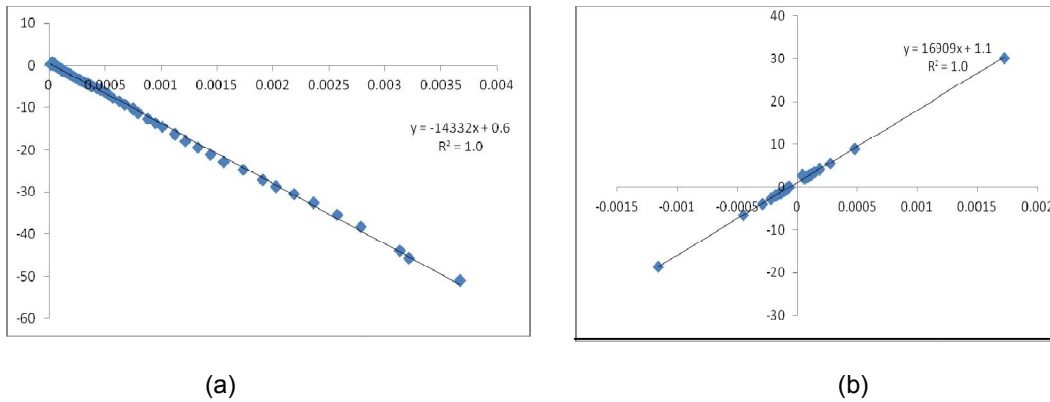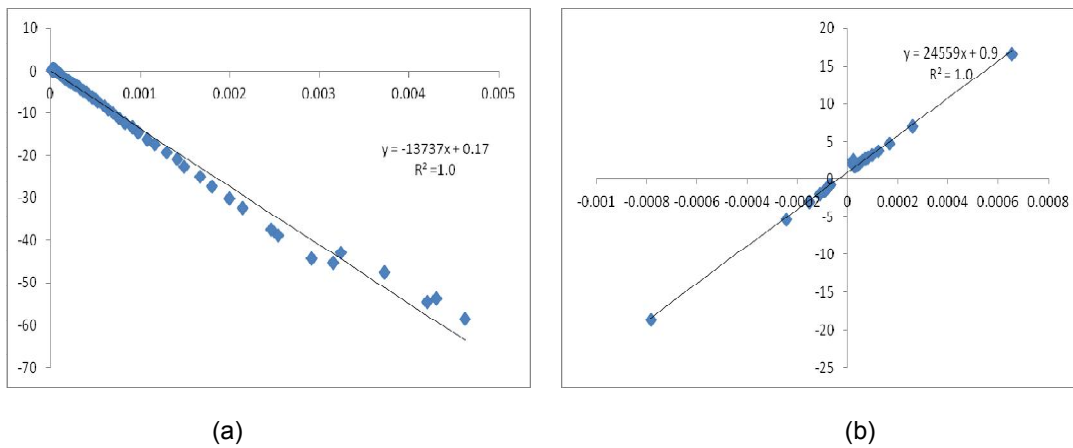


(a)                                          (b)

**Fig. A3. Sample regression curves for determination of (a) activation energy (b) reaction order of 5% NaOH cooked rice hull**

(a)                                      (b)

**Fig. A4. Sample regression curves for determination of (a) activation energy (b) reaction order of 7.5% NaOH cooked rice hull**



(a)                                      (b)

**Fig. A5. Sample regression curves for determination of (a) activation energy (b) reaction order of 10% NaOH cooked rice hull**