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ABSTRACT

Biomass is the term attributed to any renewable resource derived from organic matter that can be used in energy production. Agricultural production generates residues that are of great importance for their energy use, of which sugar cane, eucalyptus, and rice. Various residues are generated from rice cultivation, among which the rice husk and rice straw are the most important. Several thermal conversion technologies have been developed for the use of biomass in industry. Pyrolysis has been notable for its ability to produce biofuels at different stages of aggregation. The slow pyrolysis of biomass has been proposed as a pretreatment method to improve the physical-chemical characteristics of rice straw. In this process is produced, mainly, a solid called biochar, which has a higher energy content when compared to the biomass of origin. This study investigated the slow pyrolysis of rice straw at 300 - 700°C for the purpose of obtaining biochar, bio-oil, and gases for energy purposes. The experimental results show that pyrolysis temperature has important roles in yield product. The highest biochar yield was observed at a temperature of 300°C with 49.91 wt%. This represents 47% more when compared to yield at 700°C (33.87 wt.%). This behavior is linked to the proximate analysis results for fixed carbon 26.01 wt.% at 300°C. The high pH of the biochar was attributed to the presence of alkali metals, according to XRF. Thermal decomposition of the biomass resulting in a gradual increase of bio-oil (16.81 - 34.70 wt.%) and gas (6.53 - 18.05 wt.%) on a wet basis. Thus, in the dry base parameter, the bio-oil increases from 19.22 - 30.6 wt.% and the gases at 9.42-20.19 wt.%. Drying of the raw material showed, by the results, a significant increase in the co-products formed. As a consequence, we have a more efficient energy process.

Keywords: Biomass, Pyrolysis Process, Renewable Energy, Biofuel, Tar

1. INTRODUCTION

Thermochemical conversion technologies (pyrolysis, gasification, and combustion) have been developed for the use of biomass and applied in industry to produce different types of energy (Brown *et al.*, 2013; Bridgwater, 2012). Biomass is considered a potential for renewable energy sources in the future. Biomass can be categorized as agricultural waste being the only one among renewable energy resources that can be converted into an energy source (Jiang and Ellis, 2010).

The advantage of biomass in relation to fossil fuels is the low emission of sulfur and nitrogen (Carpenter *et al.*, 2014; Demirbas, 2011; Mohan *et al.*, 2006). The use of biomass as a source of renewable energy contributes to the mitigation of environmental impacts caused by greenhouse gas emissions (Jamilatun *et al.*, 2017, Lai *et al.*, 2013, Zhang *et al.*, 2012).

The pyrolysis of rice straw involves the thermal decomposition of polymer compounds, releasing organic vapors, and leaving carbon-rich solid residues (char) (Jahirul *et al.*, 2012). Pyrolytic vapors can be separated into condensable hydrocarbon compounds (oil, also known as tar) and non-condensable gases (Hosokai *et al.*, 2014).

The pyrolytic process is influenced by thermodynamic and kinetic parameters that alter the products. These parameters involve temperature, heating rate, particle size, reaction atmosphere, and residence time of the volatiles (Antal and Grønli, 2003).

Recent studies, published in the literature, bring the pyrolytic processes using rice straw (Zhang *et al.*, 2013, Chatterjee *et al.*, 2013, Huang *et al.*, 2013, Pattiya and Suttibak 2012; Fu *et al.*, 2012, Huang *et al.*, 2012, Wu *et al.*, 2012).

In this work, the use of pyrolysis is a process of thermal decomposition in the absence of oxygen or when the oxygen content is at an incomplete

combustion level (Klunk and Ponomarev, 2017; Vitali *et al.*, 2013; Zhang *et al.*, 2010). In this thermal conversion process, up to 70% of the biomass energy can be converted into a liquid product (Anex *et al.*, 2010). Fast pyrolysis is a well-studied technology that is reaching an early stage marketing (Jiang and Ellis, 2010; Effendi *et al.*, 2008). Fast pyrolysis technology has been investigated mainly for the production of bio-oil. It is typically performed using a fluidized bed to increase the heating rate (100°C / m) and at temperatures around 500°C to maximize the bio-oil yield. Higher temperatures and increased vapor residence time cause thermal cracking of hydrocarbon compounds, decreasing bio-oil yield (Klunk and Ponomarev, 2017, Zhang *et al.*, 2013, Eom *et al.*, 2013, Pattiya and Suttibak 2012). Unlike rapid pyrolysis, slow pyrolysis is carried out at a heating rate of about 5°C/min and temperature range of 300-700°C (Jamilatun *et al.*, 2017; Surahmanto *et al.*, 2017; Huang *et al.*, Wu *et al.*, 2012, Peng *et al.*, 2011).

The objective of slow pyrolysis in rice straw is the production of biochar and applicability in the soil with the purpose of increasing fertility. Biochar is responsible for increasing the retention of nutrients and water in the soil, providing the growth of microorganisms (Hossain *et al.*, 2011; Brockhoff *et al.*, 2010; Gaskin *et al.*, 2010). The amount of bio-oil and non-condensable gas products in terms of mass and energy is considerably larger than that for biochar (Kim *et al.*, 2012; Turns, 2011; Phan *et al.*, 2008).

Bio-oil is a renewable fuel or chemical feedstock, but its chemical properties are not as good as biochar due to its high water content and a large number of compounds resulting in acidity and toxicity (Agar and Wihersaari, 2012; Gómez *et al.* 2012). Pyrolytic gases are composed largely of CO and CO₂, leading to poor fuel quality.

This study presents the slow pyrolysis characteristics of rice straw to provide comprehensive information for the chemical properties and yields of the three pyrolysis products (biochar, bio-oil, and gases). The mass yield, elemental composition, and other key properties of the products were analyzed for pyrolysis temperatures of 300-700°C. Based on these results, considerations required for application of the slow pyrolysis technology to rice straw were discussed.

2. MATERIALS AND METHODS

2.1. Raw material

Rice straw was used as raw material,

coming from a farm without pre-treatment. Proximate and ultimate analyses are listed in Table 1. The analysis has been carried out in LECO elemental analyzers (CHNS-O) (FlashSmart - Thermo Scientific™) and thermogravimetric analyzer (TGA-1000 - NAVAS INSTRUMENTS™), respectively. The calorific value was measured in an isoperibolic calorimeter (C 6000 ISOPERIBOL PACKAGE 1/10 - IKA™). The chemical composition of ash (Table 2), including silica and major metal compounds, was determined by X-ray fluorescence (S6 JAGUAR EasyLoad – Bruker™). In this study, the ash content was measured by ASTM D1102-84. This requires gradual heating to 580–600°C repeated by 30 min periods until the sample weight does not change (<0.2 mg) (Jamilatun *et al.*, 2017; Surahmanto *et al.*, 2017; Huang *et al.*, 2013; Wu *et al.*, 2012; Peng *et al.*, 2011).

2.2. Low pyrolysis

Low pyrolysis experiment of rice straw was carried out at temperatures of 300, 350, 400, 450, 500, 550, 600, 650, 700°C. The details of the reactor were described elsewhere (Lee *et al.*, 2013a). Three hundred grams sample of rice straw was placed in the reactor, and the experiments were carried out with a heating rate of 5°C/min. Nitrogen was continuously supplied at a flow rate of 2.0 L/min to purge pyrolysis vapors from the reactor. Once the reactor attained the target temperature, it was maintained for 1 h for complete pyrolysis.

Pyrolytic vapors containing condensable gases (bio-oil) and non-condensable gases passed through the condensers and the gas analysis system. The connection tube from the reactor to the bio-oil condensers was heated to 400°C. The biochar and bio-oil collected after the test was collected and weighed to determine the mass yields. The composition of gases was continuously analyzed by an on-line gas analyzer for CO and CO₂. The gas yield was calculated by difference. The mass yields on a wet basis were converted into a dry, ash-free basis to evaluate the product distribution from the organic fraction in biomass. The biochar yield was also converted to an ash-free basis.

3. RESULTS AND DISCUSSION

3.1. Product yields

Figure 1 represents the yields of the slow pyrolysis of rice straw in the temperature range of 300 to 700°C, on a wet basis (Fig. 1A) and dry

basis (Fig. 1B).

On a wet basis, the biochar yield decreased with increasing temperature (Fig. 1A) ranging from 49.91 - 33.87 wt.%. This is due to thermal decomposition of the biomass, resulting in a gradual increase of bio-oil (16.81 - 34.70 wt.%) and gas (6.53 - 18.05 wt.%). The biochar yields include ash content that remained in the solid residue. In turn, the yield of bio-oil and gas have the contribution of moisture.

After the removal of moisture and ash content, the yield of the products had another behavior. Fig. 1B the biochar had a variation of 44.02 - 34.50 wt.%. Therefore, the bio-oil and gases yield varied from 19.22 - 30.6 wt.% and 9.42-20.19 wt.%, respectively. This can be results of cracking (secondary pyrolysis) of primary tar compounds by temperature and by hot char surface. Considering the significant influence of ash and moisture content in the raw material, it was desirable to convert the biochar yield to a dry, ash-free basis.

3.2. Biochar composition

Table 3 shows the properties of biochar. As the temperature of the pyrolytic process increases, the amount of volatile matter is expelled from the biomass (32.20 - 7.07 wt.%), making the material more carbonaceous (as a function of fixed carbon 26.01 wt.% at 300°C). In consequence, there is a decrease in the higher heating value from 15.80 MJ/kg to 8.77 MJ/kg, representing a reduction of 55%. The surface area (BET) increased from 3.91 to 43.39. This value is indicative of good adsorption capacity when applied to the soil. The surface area of the biochar from the 'rice straw' was relatively low when compared to the biochar of other lignocellulosic biomasses. For example, the biomass of wood and sugarcane bagasse is above 100 m²/g (Lee *et al.*, 2013a, Lee *et al.*, 2013b). The pH of the bio-oil increased from 8.75 to 11.92. The alkalinity in rice straw is due to the presence of alkaline compounds (MgO, CaO, Na₂O, K₂O) according to the X-ray fluorescence (Table 2).

3.3. Bio-oil and gas composition

Table 3 summarizes the bio-oil properties for the mean of light organic and heavy organic phases. The bio-oil compounds were in Table , according to major individual compounds. Oxygenated compounds make bio-oil unstable and reduce miscibility with hydrocarbons and calorific value (Bridgwater, 2012; Heo *et al.*, 2010). In addition, the heterocyclic compounds of the bio-oil make it viscous and easy to polymerize (Heo *et*

al., 2010-1). The water content in the bio-oil is slightly affected by the pyrolysis temperature since its yield remains in the range of 30 to 23 wt.%. Ketones are the second largest organic group in the bio-oil. Ketones are formed by condensation reactions of the fraction derived from carbohydrates and decomposition of the various oxygenates and furans. When the pyrolysis temperature is increased, cracking reactions are more severe, and lighter compounds are formed. Acid functional groups have their highest yield, and the main compound of this group is acetic acid. They can cause corrosion in subsequent processing when the equipment is made of poor quality material. In addition, organic acids are valuable by-products after separation. Therefore, the removal of acids is important for the use of bio-oil as an intermediary in the production of fuels and chemicals.

The gas fraction is composed mainly of carbon dioxide and carbon monoxide (Table 4). The yields increase with temperature due to the increase in decarboxylation and decarbonylation reactions. In addition, this fraction is also composed of small amounts of hydrocarbons (C₂-C₄). The concentration of CO increases with temperature, while that of CO₂ decreases. This is because at temperatures below 400°C the decarboxylation reactions prevail, but at temperatures above 400°C the main secondary reactions are those of decarbonylation, and therefore the release of CO is greater (Tripathi *et al.*, 2016; Tripathi, Sahu and Ganesan 2016). The yield of light hydrocarbons (C₂-C₄) and H₂ also increases with temperature due to cracking reactions. These non-condensable gases are of the low energy value in a pyrolysis process due to dilution with the entrainment gas (N₂). In addition, the low CO₂ yield is a favorable environmental feature involving the RS pyrolysis process (Stefanidis *et al.*, 2011).

4. CONCLUSIONS

Rice straw is considered a high added value agricultural residue. Slow pyrolysis is the process responsible for this energy transformation. Co-products such as biochar, bio-oil, and gases are obtained with different yields at temperatures of 300 to 700 ° C due to the pyrolytic process. The experimental results show that pyrolysis temperature has important roles in the biochar, bio-oil, and gas yield.

The highest biochar yield was observed at a temperature of 300 ° C with 49.91 wt%. This represents 47% more when compared to yield at 700 ° C (33.87 wt.%). This behavior is linked to the

results of "Proximate analysis" for fixed carbon 26.01 wt.% At 300 °C). The high pH of the biochar was attributed to the presence of alkali metals, according to XRF.

The decomposition of lignocellulosic materials directly influences the contents of volatile matter (hemicellulose and cellulose decomposition) and fixed carbon (lignin decomposition)

Thermal decomposition of the biomass resulting in a gradual increase of bio-oil (16.81 - 34.70 wt.%) And gas (6.53 - 18.05 wt.%) In wet basis. Thus, in the dry base parameter, the bio-oil increases from 19.22 - 30.6 wt.% and the gases at 9.42-20.19 wt.%. The gas yields increase the temperature increases in the 300-700°C range, with the composition being severely affected, i.e., the concentration of CO increases and that of CO₂ decreases. In addition, a slight increase in the concentration of CH₄ and C₂-C₄ hydrocarbons occurs with increasing temperature. Drying of the raw material showed, by the results, a significant increase in the co-products formed. As a result, we have a more efficient energy processes.

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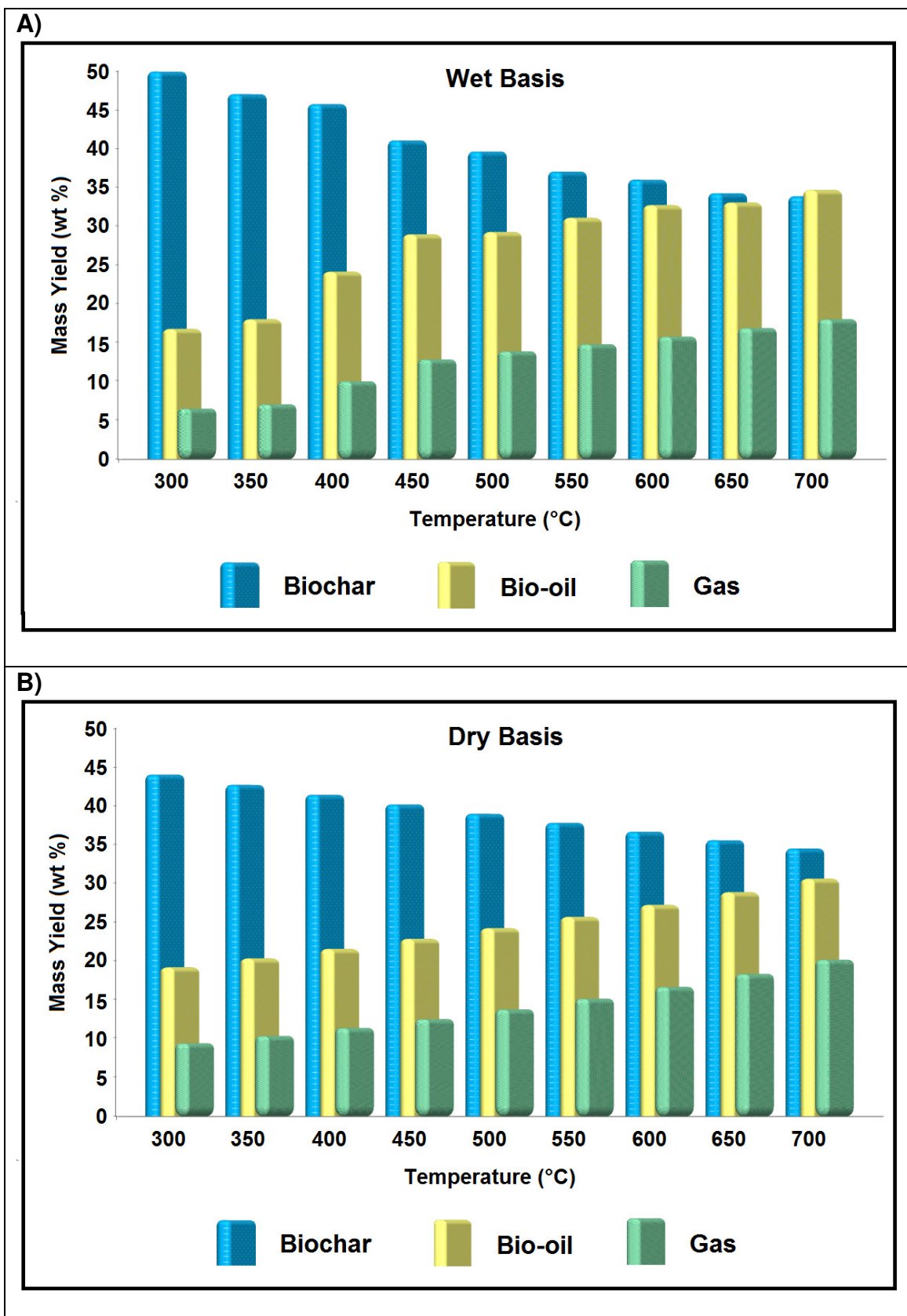


Figure 1. Product yield From slow pyrolysis of rice straw, A) on wet basis and B) dry basis

Table 1. Properties of the rice straw

Proximate analysis		Ultimate analysis	
Parameters	Weight (%) on dry basis	Elements	Weight (%) on wet basis
Volatile matter	65.71	Carbon	50.59
Fixed carbon	15.13	Hydrogen	7.02
Ash	14.29	Nitrogen	2.55
Moisture	6.41	Oxygen	48.10
HHV* (MJ/kg)	20.88		

*HHV: Higher Heating Value

Table 2. Chemical composition of the rice straw ash

Compound	Weight (%)
SiO ₂	71.82
Al ₂ O ₃	1.55
Fe ₂ O ₃	0.28
MnO	0.01
MgO	4.99
CaO	3.03
Na ₂ O	0.20
K ₂ O	0.15
TiO ₂	0.02
P ₂ O ₅	0.09
Loss on ignition	10.99

Table 3. Properties of the biochar

P.T ^a		300 (°C)	350 (°C)	400 (°C)	450 (°C)	500 (°C)	550 (°C)	600 (°C)	650 (°C)	700 (°C)
P.A ^b	VM	32.20	30.17	22.39	20.71	15.40	13.44	9.92	8.41	7.07
	FC	26.01	25.64	23.88	21.08	20.99	19.85	18.13	20.48	22.01
	Ash	35.55	36.87	39.90	41.07	46.10	47.53	49.60	50.39	52.97
U.A ^c	C	63.34	65.08	69.72	70.83	77.53	78.66	80.61	82.07	86.62
	H	3.79	3.00	2.44	2.20	1.97	1.21	1.01	0.92	0.82
	N	2.99	2.81	2.32	2.09	1.83	1.68	1.40	1.09	0.79
	O	20.81	18.90	16.73	15.05	13.92	12.62	8.83	7.53	6.98
HHV ^d		15.80	14.77	13.92	12.54	11.96	10.66	9.77	9.00	8.77
BET ^e		3.91	11.88	19.70	36.63	40.81	44.49	59.58	50.72	43.39
APD ^f		100.4	99.03	85.42	83.74	81.79	79.92	78.00	76.64	75.07
PV ^g		0.027	0.038	0.041	0.044	0.048	0.050	0.052	0.054	0.055
pH		8.75	9.10	9.55	9.93	10.10	10.99	11.15	11.30	11.92

^a Pyrolysis temperature; ^b Proximate analysis; ^c Ultimate analysis; ^d Higher Heating Value (MJ/kg-dry); ^e Surface area (m²/g); ^f Average pore diameter (Å); Pore volume (cm³/g); ¹ Volatile matter; ² Fixed carbon; ³ Carbon; ⁴ Hydrogen; ⁵ Nitrogen; ⁶ Oxygen

Table 4. Yields of the main chemical compounds in the bio-oil

Compounds	300 (°C)	350 (°C)	400 (°C)	450 (°C)	500 (°C)	550 (°C)	600 (°C)	650 (°C)	700 (°C)
Acetic acid	2.30	2.33	2.38	3.40	2.32	2.42	2.53	2.85	2.92
Propanoic acid	1.26	1.39	1.45	0.92	0.29	0.29	0.30	0.28	0.20
Formaldehyde	0.28	0.30	0.30	0.47	0.49	0.50	0.57	0.68	0.74
1-Hydroxy-2-propanone	1.98	1.77	1.58	1.32	0.89	0.72	0.43	0.31	0.22
1,3-Cyclopentanedione	3.88	3.52	3.14	2.67	2.59	1.90	0.81	0.77	0.65
2-3-methyl-2-cyclopentenone	1.34	1.30	1.19	1.18	1.38	1.31	0.42	0.36	0.29
Alkyl-phenols	2.99	3.09	3.07	3.72	3.77	3.96	6.62	6.99	7.03
Guaiacols	4.79	4.50	3.91	3.32	2.84	2.80	2.74	2.38	2.00
Catechols	1.44	2.00	2.90	3.34	3.42	3.50	3.76	4.01	4.17
2,2,4-Trimethyl-1,3-dioxalane	3.06	2.89	2.41	2.30	1.65	1.52	0.97	0.88	0.54
Carboxylic Anhydrides	1.83	1.44	1.19	1.09	1.01	1.08	1.10	1.33	1.45
Furans	4.03	4.37	4.39	4.65	5.12	4.85	4.24	4.00	3.83
Nitrogenated compounds	0.90	1.00	1.08	1.36	1.61	1.34	1.11	1.09	0.97
Water	30.92	27.99	26.32	24.27	24.52	24.61	25.21	24.54	23.12

Table 5. Influence of temperature on gas composition

Compounds	300 (°C)	350 (°C)	400 (°C)	450 (°C)	500 (°C)	550 (°C)	600 (°C)	650 (°C)	700 (°C)
H ₂	0.73	0.99	1.45	1.55	1.95	2.85	3.52	3.99	4.39
CH ₄	2.56	2.74	3.44	3.73	5.30	5.99	7.92	10.55	10.69
CO	49.31	51.35	54.41	55.49	57.20	58.86	59.30	60.51	61.88
CO ₂	55.12	54.07	52.93	50.38	47.62	45.06	40.87	38.92	35.57
C ₂ -C ₄	1.55	2.98	3.73	4.55	4.97	5.67	5.99	6.48	6.93