THERMODYNAMIC MODELING AND EXPERIMENTAL STUDY OF RICE HUSK PYROLYSIS

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Abstract

Pyrolysis of agricultural waste is a promising route for waste to energy generation. Rice husk is a type of agro-waste that is available in plenty in India. It can be used as feed for pyrolysis to produce different products such as (solid) coke and silica, (liquid) tar and other organics and syngas. HSC Chemistry computer aided code for thermodynamic modeling was used to predict the products of rice-husk pyrolysis in this research study. The pyrolysis of rice husk was carried out between 100-1200°C in the pressure range of 1 – 15 bar. The pyrolysis products predicted by HSC calculations were mainly solid coke, gases like H_2, CO_2, CO, CH_4, with small quantity of aromatic compounds like C_6H_6, C_7H_8, C_8H_{10} (ethyl benzene), C_8H_{10} (xylenes) and C_6H_5 –OH. An experimental study for product validation was also done and the results are presented.

Keywords: *Pyrolysis, syngas, HSC Chemistry, aromatic compounds.*

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1. INTRODUCTION

The main constituent of agricultural waste is biomass. Biomass primarily consists of carbon, hydrogen and oxygen along with traces of nitrogen and sulfur. Some types of biomass also contain significant amount of inorganic species e.g. silica. These inorganics form the major component of ash which varies from less than 1% in softwoods to 15% in herbaceous biomass and agricultural residues [1]. In future use of traditional carbon-based fuels such as coal, petroleum and natural gas will be limited due to depleting reserves of fossil fuels and its scarcity will be overcome by use of biomass as a major alternative source of sustainable energy to reduce global warming[2] At present, only a small fraction of the generated agro waste is used for poultry feed or as filter material while the remaining is arbitrarily dumped into fields, disposed in landfills or reused as fuel for household cooking [3]. Conventional pyrolysis is actually "slow pyrolysis" because it occurs at slow heating rate, slow heat transfer in heating zone and long residence time [4].

The main product of slow pyrolysis is bio-char which is rich in carbon content [5]. Another major product of pyrolysis is pyrolysis oil which can be used directly as fuel or added to petroleum feed stock and it may also be an important source for refined chemicals [6]. Since such liquid fuels are of greater commercial interest, some researchers in the 80's found that the liquid yield can be increased using fast pyrolysis i.e. heating the bio renewable feedstock at a rapid rate followed by rapid condensation of vapors [7]. The pyrolysis oil obtained from wood is typically a black to dark red brown liquid, having a density ~1,200 kg/m^3. The pyrolysis oil also contains water (14–33 wt%) [8].

The general composition of pyrolysis oil is as follows: cyclopentanone, methoxyphenol, acetic acid, methanol, acetone, furfural, phenol, formic acid, levoglucosan, guaiacol, and their alkylated phenol derivatives [9]. Pyrolysis process has several advantages which allow the proper utilization of the obtained products [6]. Hence pyrolysis has proved itself to be a new type of solid biomass and waste utilization technique that transforms low-energy density biomass and waste material into pyrolysis oil of high-energy density and recover higher value chemicals [10]. Numerous models have also been developed to describe the pyrolysis of biomass based on kinetic, heat and/or mass transport considerations. However these models contain parameters, which make them difficult to apply to different reactors to predict the gas product distribution.

Models based on thermodynamic equilibrium calculations [11-18] are independent of the reactor configurations. The present thermodynamic research study is done using commercial software HSC 5.11 to research the more realistic final product yield for rice husk pyrolysis.

Table 1: Proximate analysis of rice husk

Characteristics	**Value**
Moisture	6.47%
Combustible Matter	81.90%
Ash	11.71%

Table 2: Ultimate analysis of rice husk

Component	**% by weight dry ash free basis**	**Moles**
C	48.69	1
H	6.97	0.855
N	0.37	0.339
O	43.94	0.0035

2. THEORETICAL STUDY

2.1 Materials and Thermodynamic Analysis

The proximate and ultimate analysis results of rice husk are as shown in table 1 and 2

The input and output to the HSC software were as follows:

Table 3: Input and output species with pyrolysis parameters

Input species	C (solid), H_2(gas), O_2 (g), N_2(g)
Product species	CH_4(g), H_2O(g), CO_2(g), CO(g), H_2(g), C(s) C_6H_6 (g)(Benzene), C_7H_8 (Toluene) (g), C_8H_{10} (ethyl benzene)(g), C_8H_{10} (xylenes)(g), C_6H_5–OH (Phenol) (g).
Temperature Range	100˚C to 1200˚C
Pressure	1 bar, 5 bar, 10 bar, 15 bar

The product species were selected on the following basis:

Table 4: Selection of species in thermodynamic analysis

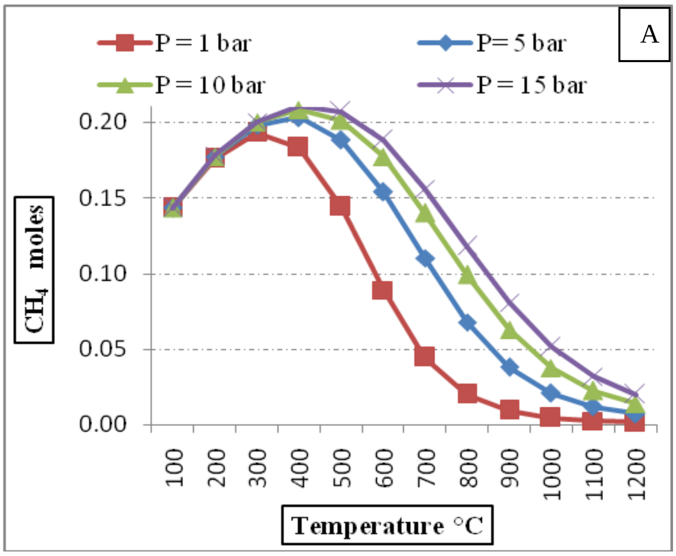
Species in pyrolysis	**Reference**
H_2, CO, CO_2,H_2O and benzene	[10]
CH_4(g), H_2O(g), CO_2(g), CO(g), H_2(g), C(s), C_6H_6 (g)(Benzene), C_7H_8 (Toluene) (g),C_8H_{10} (ethyl benzene)(g), C_8H_{10} (xylenes)(g), C_6H_5 –OH (Phenol)(g)	[19]
Phenol (g), Toluene (g), ethylbenzene (g), xylenes (g), C(s)	[20]
CH_4, CO, CO_2, C(s)	[21]
H_2,CO, CO_2, CH_4, and other light hydrocarbons, C(s)	[22]
CO, CO_2, H_2 and hydrocarbons, C(s)	[23]

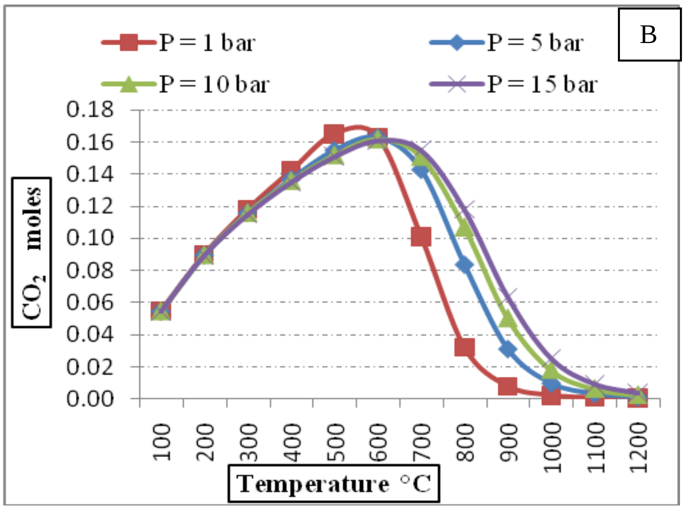
The HSC Chemistry software uses the Gibbs free energy minimization technique to predict the formation of biomass pyrolysis using the value of ultimate analysis in Table 2. The first thermodynamic calculation considered the elements C, H, O, N, S species, and but further simplified systems containing only C, H and O were investigated. The HSC calculations enable to simulate chemical reaction and processes on thermochemical basis. They utilize the principle that at equilibrium the total Gibbs energy of a system is at minimum to predict the equilibrium state [11]. The input to the system is based on one mole of carbon in feed, i.e. one mole carbon, 0.85 moles hydrogen, 0.339 mole oxygen and 0.0035 mole nitrogen. The results show the theoretical results of gas species and their fractional yeild. It is considered that the input species reached equilibrium with product species as H_2, CO_2, CO, CH_4 along with small quantity of aromatic compound gases as C_6H_6, C_7H_8, C_8H_{10} (ethyl benzene), C_8H_{10} (xylenes), C_6H_5 –OH.

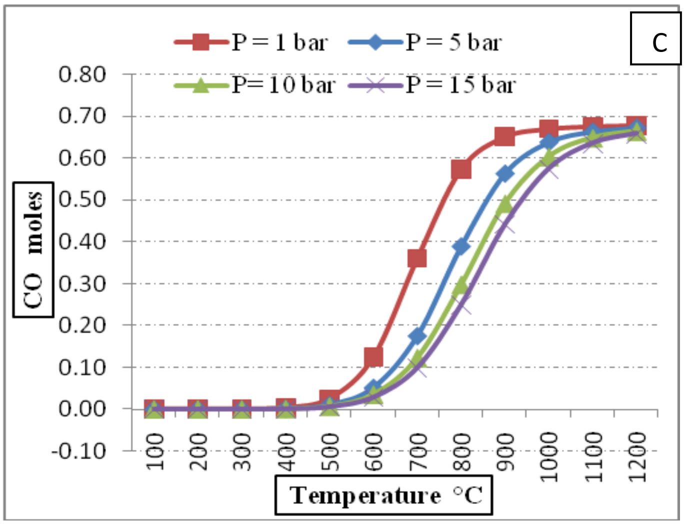
3. RESULT AND DISCUSSION

The software predicted the formation of the following products in the rice husk pyrolysis at different conditions of temperature and pressure.

3.1. Non-Aromatic Compounds







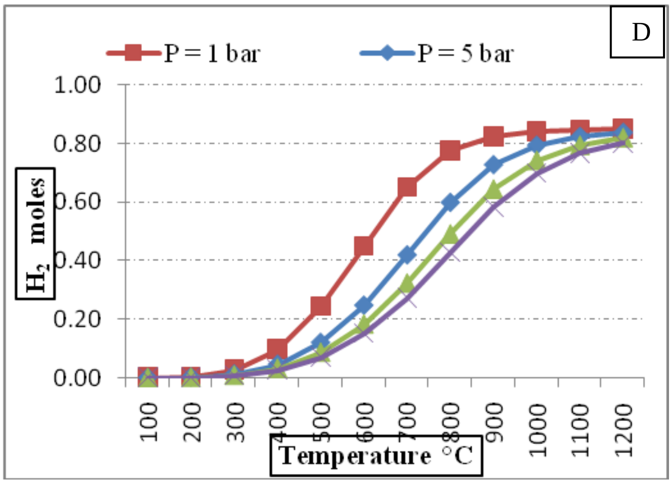
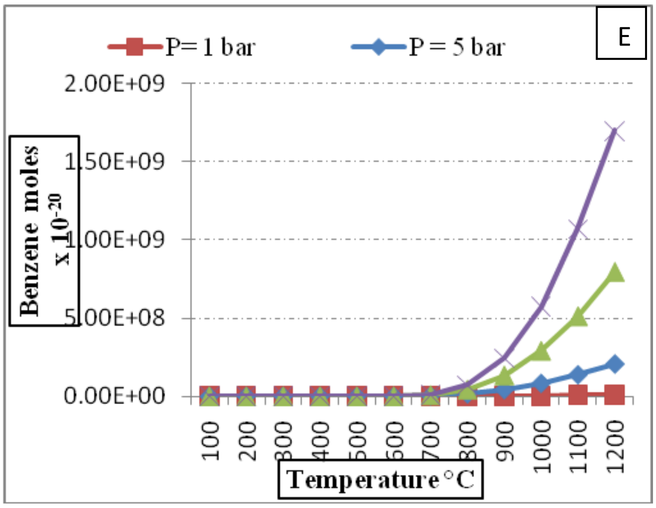
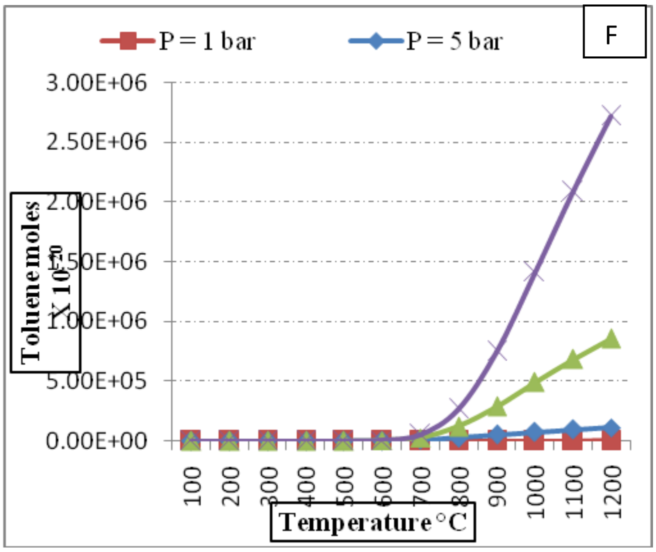


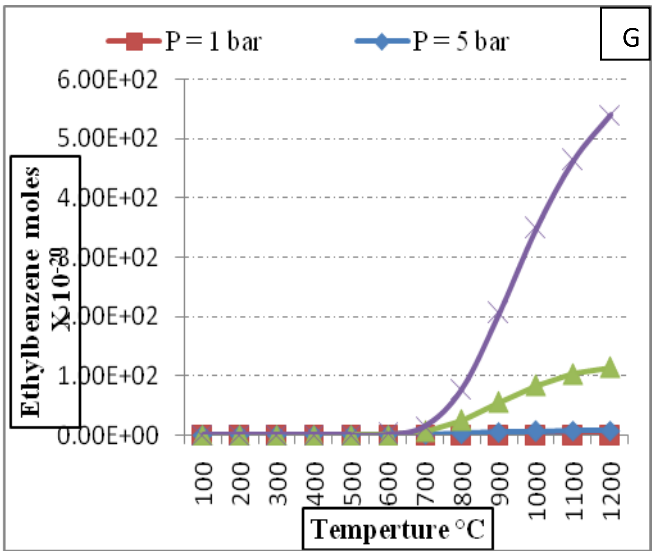
Fig 2. Moles predicted by thermodynamic model of non-aromatic components [A: Methane, B: Carbon dioxide, C: Carbon monoxide, D: Hydrogen]

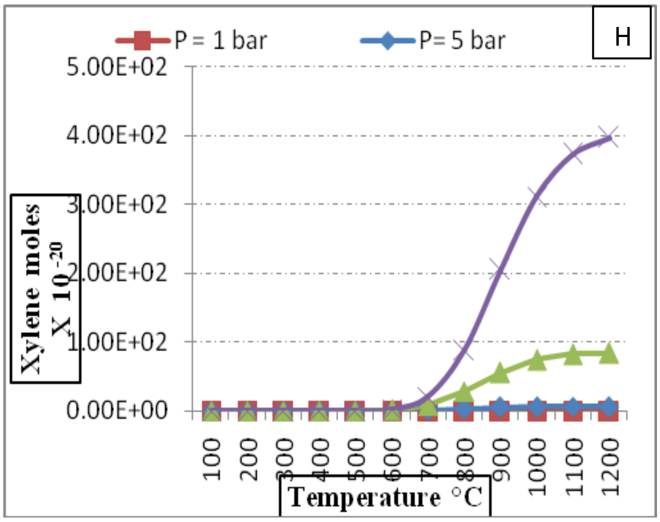
It was observed that methane and carbon dioxide formation during pyrolysis reached a maximum between 600°C to 700°C and then gradually decreased with increase in temperature at all pressures. The effect of pressure was not significant. It was observed that higher pressures favored the higher methane formation. Carbon monoxide and hydrogen formation in the product gas increased with increase in temperature but decreased with increase in pressure.

3.2 Aromatic Compounds









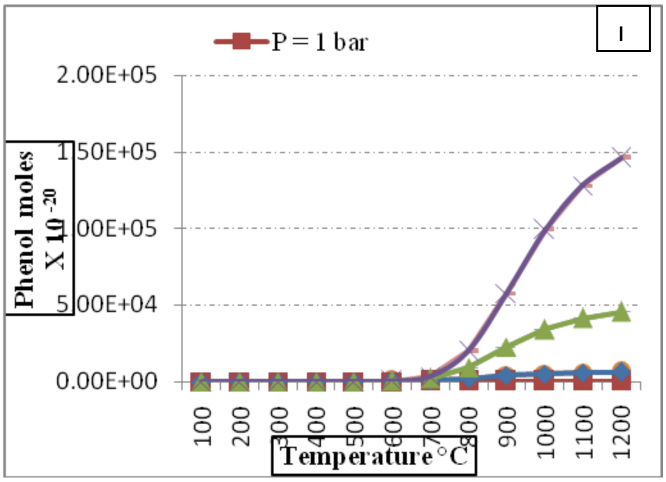


Fig 3: Moles of aromatic species.
[E: Benzene, F: Toluene, G: Ethyl benzene, H: Xylene, I Phenol]

It was observed that the equilibrium composition of aromatic components {C_6H_6, C_7H_8, C_8H_{10} (ethyl benzene), C_8H_{10} (xylenes), and C_6H_5–OH} increased with increase in temperature and pressure. According to the thermodynamic model, benzene is the most dominant product among all aromatic products produced in the pyrolysis reaction.

4. EXPERIMENTAL STUDY

4.1 Experimental Set up

The experimental runs were conducted in fixed bed reactor. An electric furnace externally heats the Inconel reactor tube. The reactor tube has a gas inlet for inert gas (nitrogen). The tube dimensions are: inner diameter 52 mm and 600 mm long, while heated zone is 500 mm.

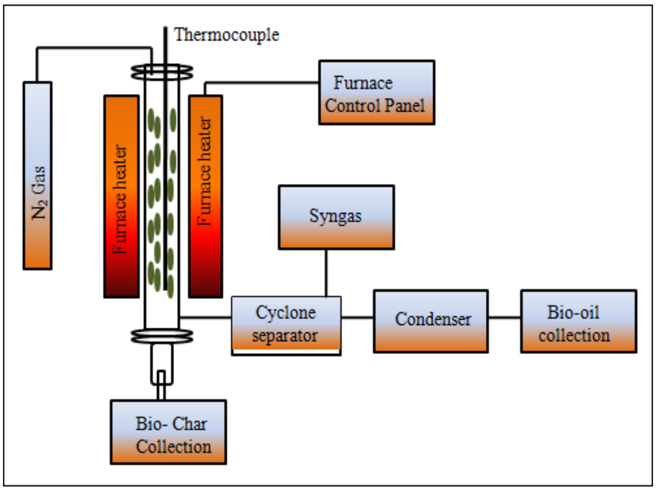


Fig 4: Schematic of Pyrolysis of Rice Husk.

4.2 Experimental Procedure

Pyrolysis experiments were carried out in nitrogen atmosphere. In this study, the inconel pyrolysis reactor was heated by a furnace with auto tuning PID temperature controller using a K-type thermocouple placed in the sample section of the furnace. The desired input flow rate of the carrier gas (N_2) was adjusted and maintained. Rice husk sample (of a fixed weight ~ 75 gm) was initially placed in the pyrolysis reactor. The input flow rate of N_2 gas was adjusted and the sample heated to 400°C. The temperature was measured using calibrated thermocouples. When temperature inside the reactor reached 400°C, the temperature was maintained for ~2 hours. The products of the pyrolyser were discharged in a gas solid separator and then passed through a chilled water condenser. The liquid products were collected in the end of the experimental run while the gaseous products were analyzed using a online gas analyzer. Similar experimental runs were carried out at 650°C and also at high pressure (4 bar).

Table 5: Rice husk pyrolysis at corresponding reaction condition

Biomass	Initial feed weight	Optimum operating Temperature	Pressure	Residence time
Rice husk	75 gm	400°C	1 bar	120 min
Rice husk	75 gm	650°C	1 bar	120 min
Rice husk	75 gm	400°C	4 bar	120 min

4.3 Product Yield

Products obtained from pyrolysis process are liquid - pyrolysis oil, solid char, and syngas. Figure 5 shows the solid and liquid product yield obtained in experimental studies.

Fig 5: Product yield of pyrolysis of Rice husk.

4.4 Effect of Temperature

The experimental results showed that the liquid yield decreased with increase in reactor temperature from 400°C to 650°C may be due to the secondary cracking reaction of pyrolysied oil vapors. The cracking of vapors is favorable for increase in gas yield and decrease liquid yield. A decrease in char yield was also observed at higher temperature. It was also observed that, the carbon and nitrogen percentage increased in solid char at 650°C than 400°C while the hydrogen and sulfur content decreased. Table 6 shows the CHNS analysis of solid char.

Table 6: CHNS analysis of Bio char

Elements	At 1 bar Pressure 400°C	650°C
C	46.42 %	54.21 %
H	2.188 %	2.754 %
N	0.593 %	1.419 %
S	0.015 %	0.032 %

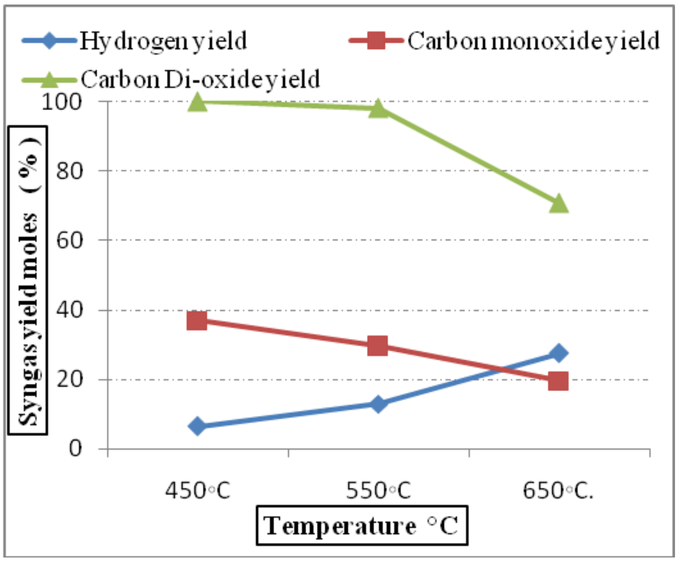


Fig 6: Syngas yield at different temperature

4.5 Effect of Pressure

It was seen that the high pressure (4 bar) was favorable for increase in liquid yield. The result showed that upto 36.84 % increase in liquid pyrolysis oil was observed with increase in Pressure.

Table 7: Effect of pressure on rice husk pyrolysis at corresponding reaction condition

Feed	Product yield (At 400°C) 1 bar	4 bar
Rice-husk (Initial Wt = 75 gm)	Combustible Char 50 gm Combustible Liquid 12 ml.	Combustible Char 51 gm Combustible liquid 19 19 ml

4.6 FTIR Analysis of Pyrolysis Oil

The FTIR analysis of pyrolysis oil was also done. Figure 7 and 8 and table 8 show the FTIR analysis report. It was observed that there was an increase in the number of functional groups in the pyrolysis oil at higher pressure.

Table 8: Functional group present in Pyrolysis oil

Wave number (Frequency) cm^{-1}	Group	Class of compound [24]	Experimental determination 1 bar	4 bar
3650-3100	O-H stretching	Polyrimic O-H water impurities		3318.17
3000-2800	C-H stretching	Alkanes	2852.71 2921.42	2915.54
1775-1680	C=O stretching	Ketones, Aldehyde, Carboxylic acid		1672.53, 1724.63
1575-1425	C=C stretching	Alkenes	1458.56	1442.69
1425-1325	$-NO_2$ stretching	Nitrogenous compound		1337.37
1300-1175	C-H Bending	Alkanes		1233.26
1150-1000	C-O stretching O-H bending	Primary, secondary, Tertiary alcohols, Phenol, Ester and Ether		1007.42
950-875	C-H bending	Alkynes		
900-650		Aromatic compound		830.82

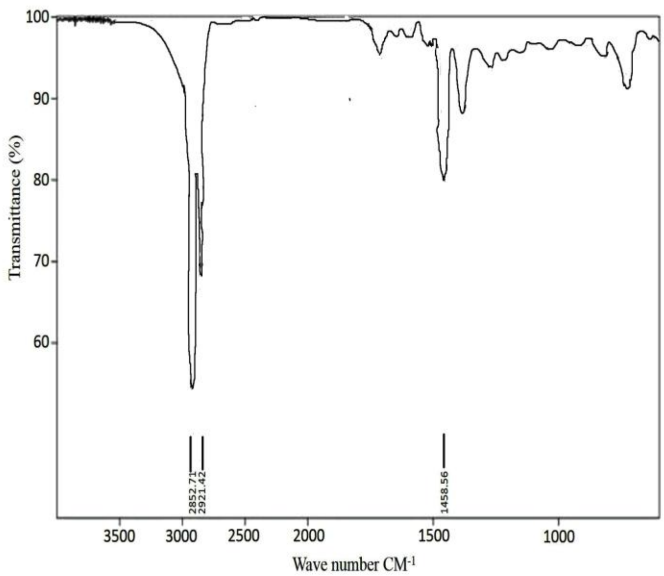


Fig 7: FTIR analysis at 400°C and 1 bar

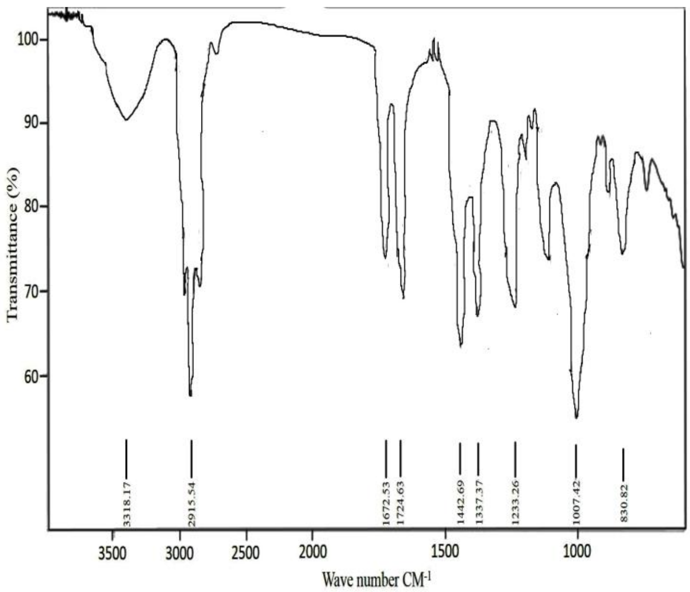


Fig 8: FTIR analysis at 400°C and 4 bar

5. CONCLUSION

The thermodynamic analysis of rice husk pyrolysis showed the formation of different compounds in the system. The products were aromatic and non-aromatic in nature. The analysis indicates that aromatic fraction is not present in significant quantities in the equilibrium mixture. According to the results, the system has a high tendency to move toward thermodynamically stable species such as CH_4, CO_2, H_2O, CO, H_2, and C at equilibrium. A conjecture as a result of our analysis is that the aromatic products in the pyrolysis occur before the system actually reaches thermodynamic equilibrium. Therefore, these aromatic products can be treated as intermediates that eventually convert to more thermodynamically stable species as the system reaches equilibrium. Pyrolysis at high pressure favours liquid oil production, where increasing in temperature increases syngas yield and decrease in char.

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