Bio-Oil From Rice Straw By Pyrolysis: Experimental And Techno -Economic Investigations.

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Abstract: The use of biomass as a source of energy is gaining increasing interest in both developed and developing countries as a renewable source of energy and to avoid the environmental hazards associated with open burning of ligno-cellulosic materials. This work is concerned with the fast pyrolysis of rice straw which is generated seasonally in enormous quantities to produce biooil which could replace fuel oil #2. Experimental investigations on a pilot-scale in an entrained flow reactor demonstrated that the biooil produced is of acceptable characteristics and has a calorific value of about 29kJ/kg. Process design has been developed for a 200 ton/day commercial facility. Material and energy balance and basic engineering have been accomplished using ASPEN PLUS. Techno-economic investigations have been conducted and financial analysis has been performed using ASPEN ICARUS. Results indicated that for a Base Case, the Fixed Capital Cost is about US $ Million 7.6 and for a pessimistic selling price of US $ 0.13/kg, the Internal Return of Return (IRR), exceeds 43%. Sensitivity analysis indicates that even for increase of the Fixed Capital to about US $ Million 10.9 the IRR still exceeds 30%. Further work is needed for technological development and for ensuring processing over the year round using other ligno-cellulosic materials.
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1. INTRODUCTION

Enormous quantities of agricultural wastes are generated annually worldwide. Some useful applications of biomass such as animal fodder, fertilizer, paper making, source of energy in rural stoves and panel boards are widely adopted. However, large quantities are disposed of sporadically causing severe environmental problems. One of the most problematic agriculture wastes is rice straw which is generated in huge amounts over a limited harvesting period. In Egypt the quantity of rice straw generated annually exceeds 3 million tons. Its high content of silica limits its direct application as animal fodder, in paper making and as a solid fuel. Thus, farmers proceed towards its immediate disposal, even through open burning, despite the stringent regulations banning this practice, for its serious health hazards, to prepare the land for the next crop. On the other hand, the depletion of petroleum, natural gas and other conventional fuel sources is motivating researchers to develop new renewable sources of energy. The use of biomass as a source of energy is being widely addressed as reported by EERE [1], Bridgewater [2] and Mullaney[3] . Of specific concern is the production of biooil by fast pyrolysis as addressed by Ringer [4] and Dynamotive [5]. Investigations on the preparation of biooil from rice straw have been reported by Putun [6], Islam [7], Wang [8] and Tu [9] Several fast pyrolysis reactor configurations exist today including ablative reactors, entrained flow reactors, rotating core reactors, vacuum pyrolysis reactors, circulating fluidized bed reactors, and deep bubbling fluidized bed reactors Mullaney [10]. Fast pyrolysis on a near-commercial status has been reported in Canada and UK Bridgewater [11], Finland Oasmaa [12] and the Netherlands Venderbosch [13]

Various techno-economic analyses of fast pyrolysis plants are available in the literature. Prior investigators estimated bio-oil production costs to range between US$ 0.11 and $0.32 per litre Ringer [4]. Other investigators Mullaney [10] developed economic model for bio-oil plants for 100, 200 and 400 ton /day wet wood plant. Cost per litre was estimated to be about US$ 0.34, US$ 0.26 and US$ 0.22 for the above mentioned capacities respectively. Also, Brigdwater (2009) has carried an analysis of several plants around the world out and updated their data to 2008 to develop generalized short-cut equation for the capital cost including all design, equipment, construction, civil work and commissioning.

The analysis in this work is based on experimental and published work, in particular; the National Renewable Energy Laboratory (NREL) report by Ringer [4] for a 550 dry ton/day plant producing 28 million gallons of bio-oil per year at a cost of US$ 0.17 per litre. This analysis includes the detailed techno-economic study of pyrolysis technology from wood.

This paper is concerned with the production of bio-oil from rice straw by fast pyrolysis. Experimental studies on bench-scale have been conducted, oil characteristics have been identified and engineering data for the design and techno-economic assessment of a full-scale facility of 200 ton / day biomass (rice straw) dry basis have been developed.

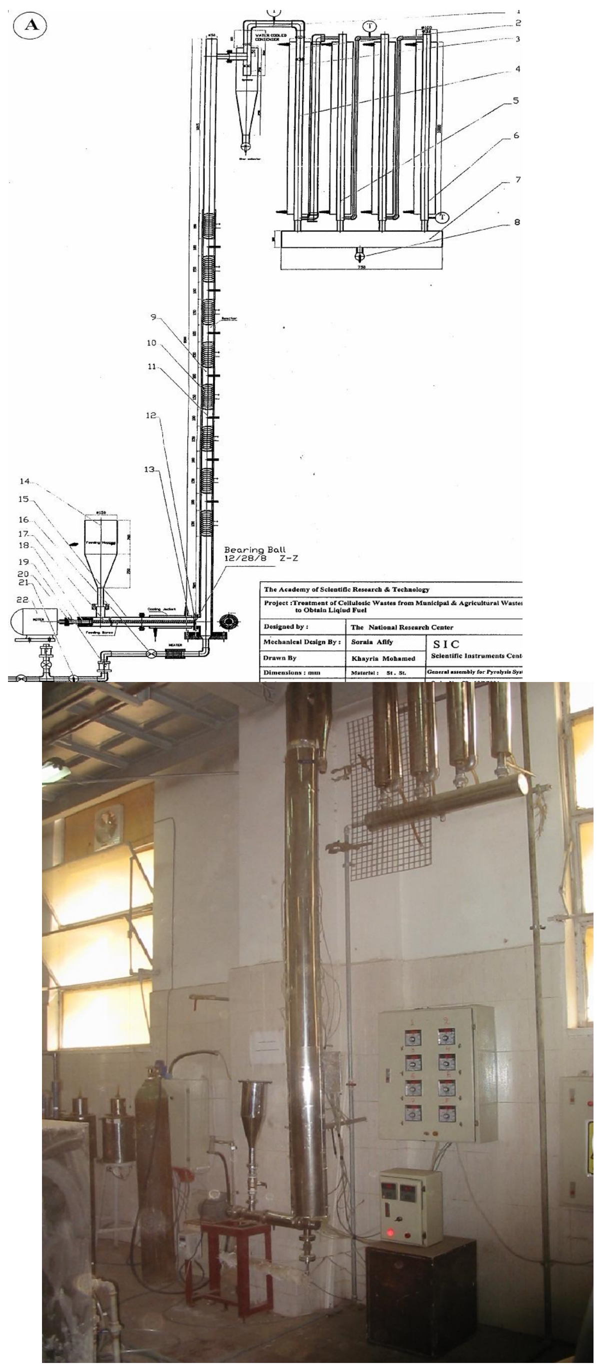
2. EXPERIMENTAL

2.1 Material and Methods

The reactor used is the entrained flow type in which heat is transferred to the pyrolysing biomass particles from the hot gases by convection. A bench scale set-up has been designed, constructed and tested. The set-up comprises the followings:

A feed vessel, a screw conveyor for feeding the straw to the bottom of an entrained flash pyrolyser flow reactor operating at atmospheric conditions and using nitrogen gas as a carrier medium .The gas is preheated before being introduced into the bottom of the reactor. The reactor is made of stainless steel with about 50 mm diameter and 3500 mm height. Eight temperature controlled electric heaters of 0.2 kW each provided the heat required for biomass pyrolysis. The pyrolysis products pass through a cyclone to collect the char before being quenched in a double pipe- cooler to condense the bio-oil while the non-condensable volatiles are released. The set-up is provided with the necessary instruments to follow- up temperatures and rate of flow. The experimental set-up is depicted in Figure 1.

Fast pyrolysis experiments have been conducted using milled rice straw of particle size 1-2 mm at temperatures in the range 450 to 600°C. The capacity of the experimental set-up is about 1 kg/hr (batch fed with about 25 gm every about 2 minutes). Nitrogen flow has been in the range of 15 to 30litres/min. The residence time of the volatile matter is around 1-5 s.



1-cyclone cooler/condenser, 2- reactor/ cyclone connection, 3-cyclone, 4, 5, 6-1st, 2nd, 3rd 4th cooler/condensers,
7, 8-condensate collectors and accessories, 9- reactor, 12-sleeve, 14-feeding hopper, 17-screw,

Figure1. Experimental set-up for fast pyrolysis of rice straw

2.2 Characterization

a) Rice Straw Characterization

A sample of newly harvested rice straw was washed, dried and milled and laboratory analyzes for moisture content and water soluble materials. The weight percentage composition as determined according to standard procedures is provided in Table (1).

b) Bio-oil Characterization

The collected bio-oil has been characterized through measurement of the following:

a) Elemental composition using Vario El Elementar Analyzer

b) Calorific value using IKA-C 2000.

c) Types of functional groups by Fourier Transfer Infra Red FTIR using JASCO FT/IR 300 Fourier Transfer Spectrometer N

d) Structure of organic compounds by Proton Magnetic Resonance Spectroscopy 1H-NMR using Jeol-Ex-270 NMR Spectrometer

2.3 Results

2.3.1 Rice Straw characteristics

Typical composition of rice straw samples used in this work is presented in Table (1).

Table (1) Analysis of Egyptian rice straw (on dry basis)

Rice Straw Component	%
Pectic substances	2.3
Holocellulose	71
a) α-cellulose	34.94
b) hemicellulose	36.06
Lignin	12.3
Soluble materials	14.17
Total	100
Ash	18.5

2.3.2 Bio-oil Characteristics

The elemental composition of the bio-oil as collected at different pyrolysis temperatures using Vario El Elementar Analyzer is presented in Table 1. Average values are almost in agreement with reported data. Highest carbon content and H/C molecular ration is at pyrolysis temperature 550° C.

Table (2) Elemental Analysis of Bio-oil Samples at Various Pyrolysis Temperatures

Temperature C	C%	H%	N%	O% (by difference)
450	49.939	3.877	2.473	43.711
500	47.419	3.344	2.556	46.681
550	54.122	9.55	1.761	34.567
600	47.41	3.744	1.791	46.29
Average	49.723	5.129	2.337	42.812
Reported Average Bridgewater (1999)	44-47	6.50	0-0.2	46-48

The calorific value has been found to have an average value of about 29kJ/kg. This is in agreement with data for bio-oil from rice straw published by Putun [6] which is relatively higher than average reported data by Bridgewater [3] for bio-oil from other biomass (22kJ/kg). Results of the H- NMR and FTIR are depicted in Figures (2) and (3) and Table (3). These results indicate the existence of following:

- Hydroxides at wave length 3150-3600 cm-1
- Esters and carboxylic acid derivatives at wave length 1720-1780 cm-1
- Methyls and methylene groups at wave length 2930-2980 cm -1
- Aromatic compounds at wave length 700-900 cm -1
- Amines at wave length 2361cm-1 for biooil prepared at 500-600 but not at 450oC indicating that amines are not formed at lower temperatures.
- The H- NMR confirmed the presence of the phenyl, phenolic, ethanol, methyl and methylene groups

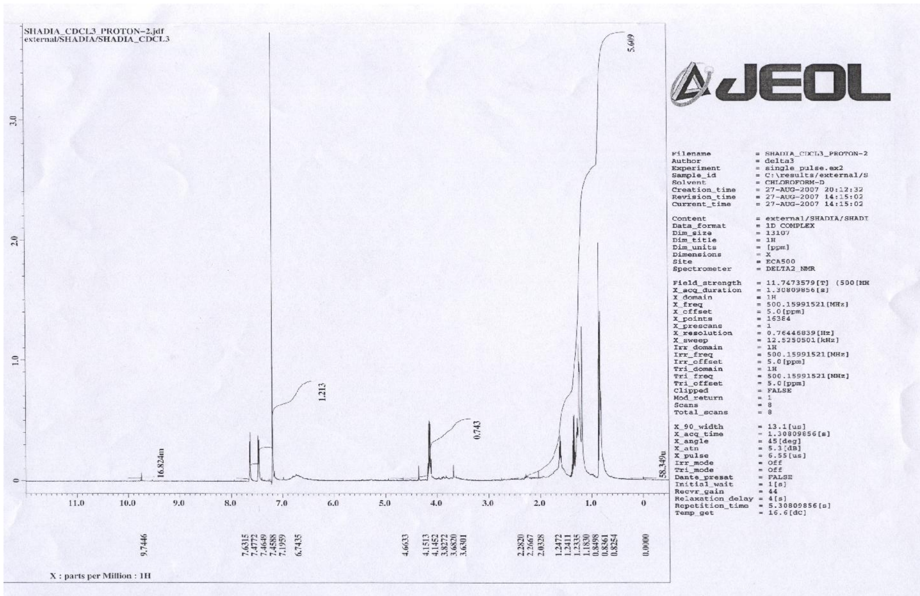
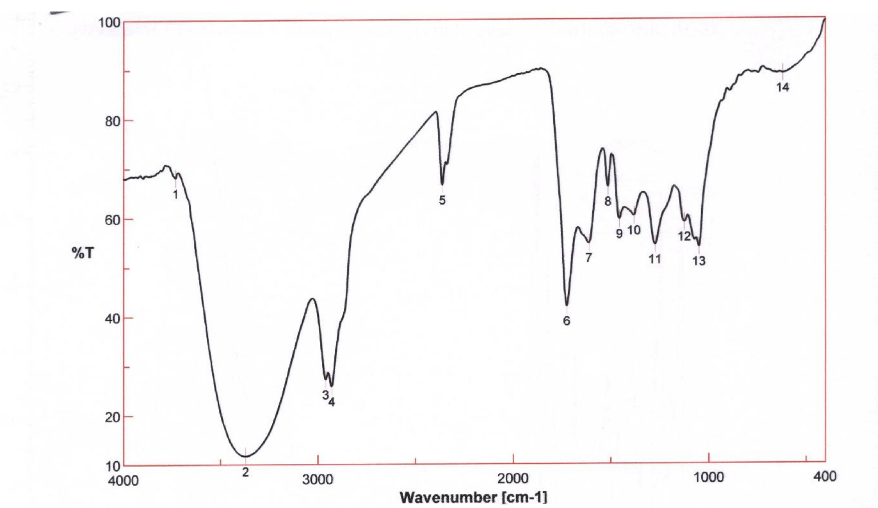


Figure (2) Results of H- NMR for biooil produced at 550 ^{o} C



Accumulation	16
Resolution	4 cm-1
Zero Filling	ON
Apodization	Cosine
Gain	Auto (2)
Scanning Speed	Auto (2 mm/sec)
Date/Time	19/08/2007 1:24ā
Update	19/08/2007 1:25ā
Operator	
File Name	550
Sample Name	550
Comment	

No.	cm-1	%T	No.	cm-1	%T	No.	cm-1	%T
1	3730.62	68.1239	2	3370.96	11.7136	3	2960.2	27.2473
4	2928.38	25.8637	5	2361.41	66.5719	6	1725.01	41.9866
7	1612.2	54.7462	8	1514.81	66.1211	9	1455.99	59.5721
10	1381.75	60.2554	11	1273.75	54.3938	12	1125.26	58.9617
13	1050.05	53.9292	14	620.002	88.9592			

Figure (3) FTIR for bio-oil produced at 550 ^{o} C

3. PROCESS DESIGN OF PROPOSED COMMERCIAL FACILITY

The process design of a production unit processing 200 ton/day rice straw has been developed. This capacity has been selected guided by a demonstration commercial facility for the production of biooil from ligno-cellulosic materials (Dynamotive [5]. Design indicators have been based principally on the results of undertaken experimental investigations as outlined in section 2 and complemented by published data reported by Ringer [4] and others. Since bubbling fluidized bed is the recommended reactor for implemented facilities, it has been adopted in this work. The process design for the fast pyrolysis process essentially comprises the following stages:

3.1 Rice Straw Handling and Preparation

Bales of rice straw are opened and transferred to the milling area using a set of appropriate conveyors. The straw is then passed below a magnetic separator before it is directed to knife mills. The milled straw is then sieved using mechanically vibrating screens with 2mm openings. The milled straw of size <2mm is then fed to a storage bin equipped with rotary air locked feeder to ensure the regular and steady feed to the pyrolyzer.

3.2 Fast Pyrolysis in a Fluidized Bed Reactor

The bubbling fluidized bed reactor contains a bed of silica sand which is fluidized using clean gases produced from the pyrolysis as well as inert nitrogen gas. The milled rice straw is introduced at the bottom of the reactor where it is mixed with the hot agitated sand particles and transformed to three basic phases:

§ A solid phase comprising small carbon particles and ash (char)

§ Condensable vapours which essentially constitute the biooil product

§ Non- condensable gases

The fluidized silica sand, which withstands a temperature of about 1500 ^{o}C and is in a state of continuous turbulence, promotes fast and homogeneous heat transfer to the rice straw particles ensuring high efficiency of the pyrolysis process and the continuous and rapid evacuation of the produced vapours. The reactor is indirectly heated using the gases produced from the char burning, as described below, as well as the non- condensable gases which have been cleaned using electrostatic precipitator and are burnt in the pyrolyzer to get rid of all combustible matters. The fast pyrolysis process is completed in about 1-5 seconds at 450-550 ^{o}C.

3.3. Solid Phase Separation and Combustion

The char is separated from condensable vapours and gases in high efficiency cyclones and is temporarily stored before being directed to a combustor using pneumatic conveyor. The char is combusted at about 1600-1800 ^{o}C and the hot gases are used for heating the pyrolyzer.

3.4 Bio-oil Cooling and Storage

After separating the char, the condensable vapours and non-condensable gases are cooled to about 100 ^{o}C by a condenser using chilled water at 4 ^{o}C. The condensed vapours are further cooled to about 40 ^{o}C to form the bio-oil which is then stored.

3.5 Cleaning and Reusing the Non-Condensable Gases

After condensing the bio-oil, the resulting gases and residual vapours are directed to electrostatic precipitators before being reused in the fluidized bed reactor.

The proposed fast pyrolysis process is depicted in Figure (4).

4. SIMULATION SOFTWARE

The process has been simulated using ASPEN PLUS 2006.5 from ASPENTECH. Detailed material end energy balance has been developed. The physical data for the components was obtained either from the ASPEN inhouse databank or from literature. Equipment sizing and basic engineering have been developed manually for capital cost evaluation. Figure (3) presents process flow sheet as depicted by the program for selected processing areas while table (2) presents basic equipment blocks utilized in the simulator.

4.1 Design Basis

The production of bio-oil from rice straw was modelled using various assumptions. Table 1 summarises key design parameters.

5. TECHNO-ECONOMIC INDICATORS

Techno-economic indicators have been developed under Egyptian conditions as a case study.

5.1 Basis of Cost Estimates

Equipment costs have been obtained from ASPEN ICARUS whenever available. Other equipment costs have been obtained from other published sources, such as Peter's et.al [15], as updated to 2007 using Marshal and Swift cost index. ASPEN ICARUS was also used for estimating material cost as well as installation cost for nearly all equipment used in the process. ASPEN ICARUS was also used to for estimating material and installation cost for auxiliary equipment such as piping, insulation, electrical... etc. Manpower, utilities and raw material costs have been estimated using current Egyptian market prices. Biooil sales price has been assumed to be about US$ 0.13/kg which is 30-40% of the price of fuel oil #2 on international market as of August 2008.

5.2 Results

Financial Analysis has been conducted using ASPEN ICARUS 2006.5.Table (4) shows the distribution of equipment costs among the processing stages while Table (5) presents the breakdown of capital costs.. Elements of fixed capital costs have been analyzed to take into consideration the possibility of probable variations. Accordingly, four scenarios have been developed. Table (6) shows rice straw fast pyrolysis annual operating cost based on 200 ton / day plant size for Scenario I. Estimates for the four Scenarios as presented in Table (7) and Figure (5). The sales price of biooil which provides an Internal Rate of Return (IRR) of 10% which is the current prevailing discount factor has been estimated as presented in Table (7).

Results indicate that the IRR for the Base Case exceeds 43% for Fixed Capital Cost of about US $ Million 7.6. However, the IRR remains about 30% if the Fixed Capital Cost increases to about US $ Million 10.9 as depicted in Scenario IV.

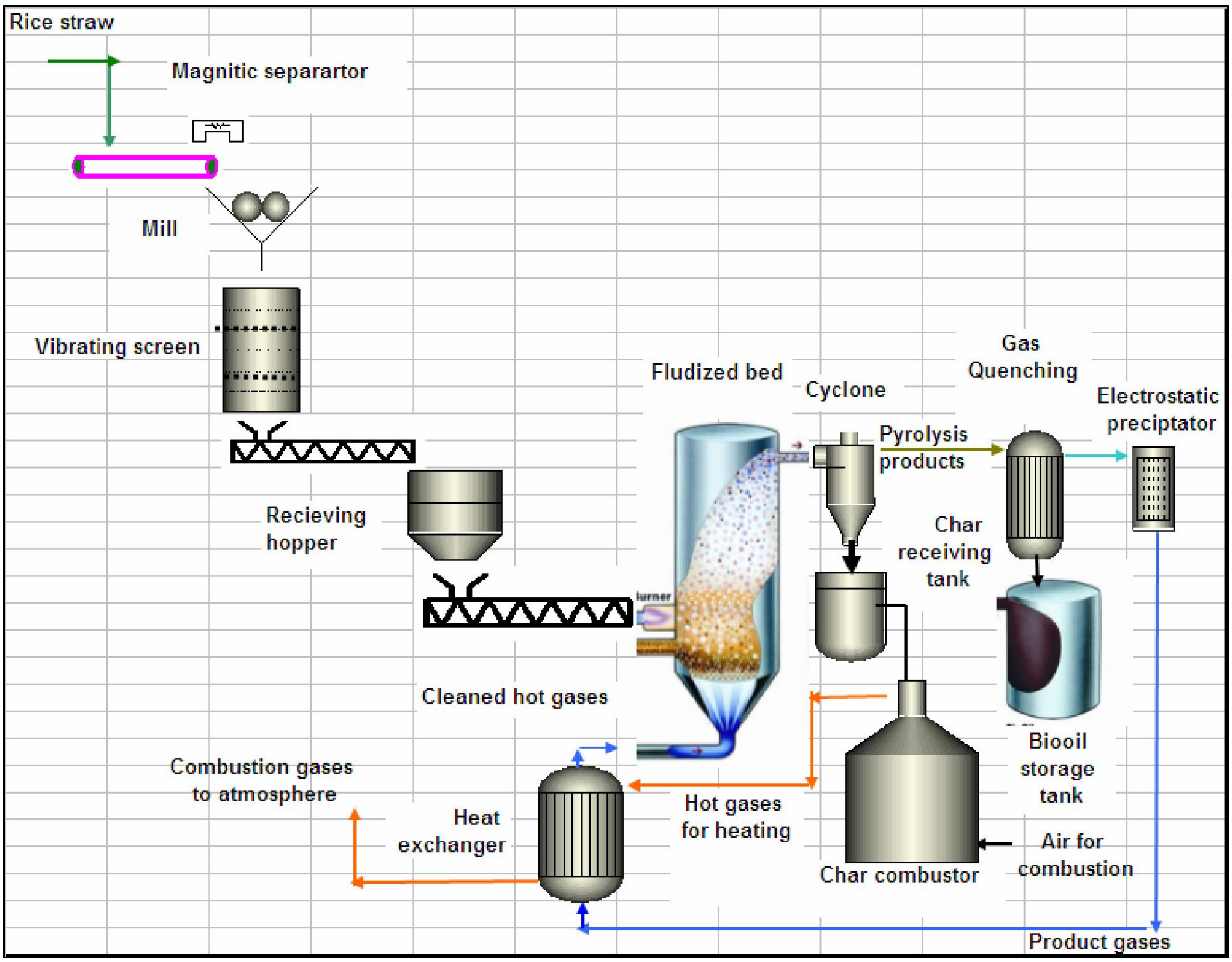


Figure (4) Process Flowsheet of the Proposed Pyrolysis Facility

Table (3) Key Design Parameters for Bio-oil Production

Parameter	Value
1. Feedstock	
Type	Rice straw
Moisture content	8-10%
Throughput	200 ton / day
Particle size	2 mm
2. Pyrolysis design	
2.1 Reactor	
Pyrolysis type	Bubbling fluidized bed
Pyrolysis temperature	550◦C
Pressure drop across the reactor	5 KPa
Input pressure	30 KPa
Retention time	1-6 seconds
Feed	833 kg / hr
Ground Particle size	2 mm
2.2 Gases	
Carrier gas	2.75 kg gas / kg feed *
2.3 Bed material	
Type	Silica sand
Particle size diameter	1 mm
Density	3.4 g /cm3
3. Yield %	
Oil	27
Char and ash	27
Gas	26
Water and others	20

*Nitrogen gas is used for process start up, for steady state operation recycled clean gases are used in fluidized bed pyrolyser

Table (4) Distribution of equipment cost among processing stages

Stage	**%**
Rice straw handling and preparation	19
Pyrolysis reactor	25
Product recovery and storage	21
Heat recovery	35
Total	**100**

Table (5) Distribution of Capital Costs components

Item	**%**	**Remarks**
Purchased Equipment	100	Of Purchased Equipment
Equipment Installation	30	Of Purchased Equipment
Piping	15	Of Purchased Equipment
Civil	15	Of Purchased Equipment
Steel	15	Of Purchased Equipment
Instrumentation	10	Of Purchased Equipment
Electrical	10	Of Purchased Equipment
Insulation	8	Of Purchased Equipment
Paint	8	Of Purchased Equipment
Other	10	Of Purchased Equipment
Engineering	10	Of Total Project Costs
Contract Fee	5	Of Total Project Costs
Contingencies	10	Of Total Project Costs
Total Project Costs		

Table (6) Rice Straw Fast Pyrolysis Annual Operating Cost $ (Scenario I)

	Item	Cost ($)
Operating Costs $		**1,068**
1	Raw Materials	390
2	Utilities	470
3	Operating Labor and Supervision	55
4	Maintenance Labor	154
Fixed Costs – Depreciation		**427**
Plant Overhead		**10**
General and Administrative Costs		**120**
Total Annual Production Costs		**1,626**

Table (7) Financial Indicators for Proposed Scenarios

Item	I	II	III	IV
Capital Costs (US $ Million)	7.64	8.55	9.27	10.91
Annual Production Cost (US $ Million)	1.63	1.71	1.75	1.87
IRR % @ US$ 0.13/kg biooil	43.5	39.4	35.7	30
Net Present Value (US$ Million)	17.84	16.85	15.99	14.16
Price of Biooil for IRR 10 %	0.058	0.061	0.064	0.069

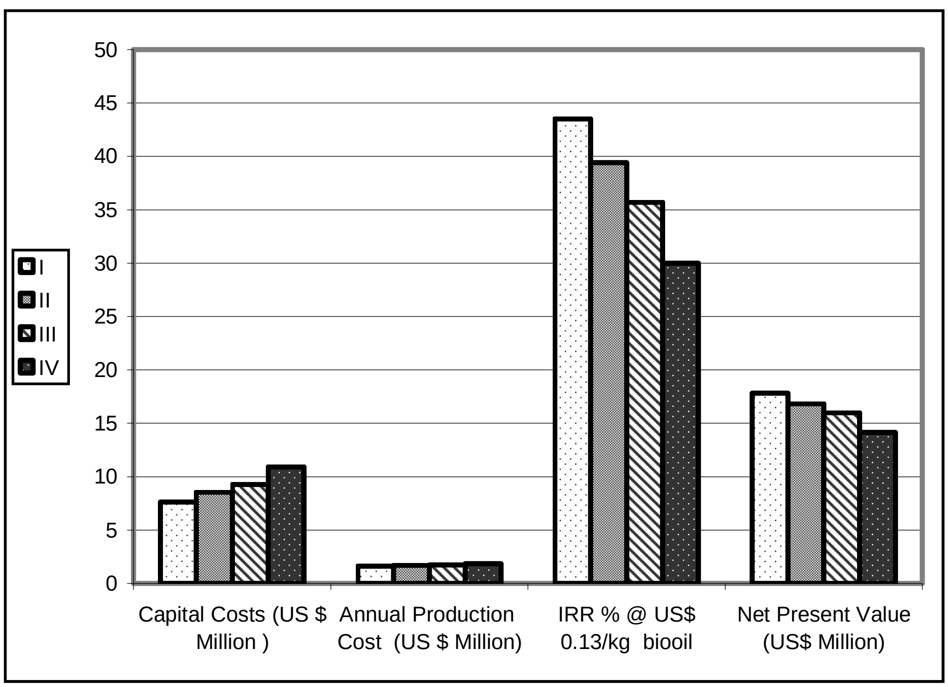


Figure (5) Results of Financial Analysis for Proposed Scenarios

5. CONCLUSIONS

Bio-oil with adequate characteristics has been produced by fast pyrolysis of rice straw which is currently an environmental nuisance. Experimental results indicate that bio-oil with relatively high yield could be could be obtained at 550^o C. The produced bio-oil has composition of 54% C, 9.55% H_2, 1.76% N_2 and 34.56% O_2 with calorific value of 29 kJ/ kg. Based on process design and basic engineering for an integrated scheme, techno-economic appraisal indicated that the process is viable. However, production facilities have to take into consideration storage and transport requirements. Also, it is necessary to ensure steady production using other ligno-cellulosic materials along the whole year.

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