

## COMPARISON OF YIELD AND FUEL PROPERTIES OF THERMAL AND CATALYTIC CALOPHYLLUM INOPHYLLUM SEED SHELL PYROLYTIC OIL

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### ABSTRACT

In this work, the production and evaluation of fuel properties of pyrolytic oil from calophyllum inophyllum seed shell was reported. The elemental analysis were applied on the raw material to know the percentages of fixed carbon, volatile matter, ash content, moisture, carbon, hydrogen, nitrogen, oxygen and etc. The TG-DTG analyses were applied on the raw material to investigate the thermal degradation. Both thermal and catalytic pyrolysis using  $\text{Al}_2\text{O}_3$  was carried out. The aim of the study was to detect the optimum particle size for thermal pyrolysis and feed to catalyst ratio for catalytic pyrolysis to produce maximum pyrolytic oil also to increase the quality of oil using catalyst. The CI seed shell particle sizes of 0.7, 1.16 and 2.36mm was studied. Maximum yield of 41% wt. of oil was obtained in the particle size 2.36mm. The catalytic effect of  $\text{Al}_2\text{O}_3$  on CI seed shell pyrolysis at a feed to catalyst ratio of 6:1, 8:1 and 10:1 was studied. Maximum yield of 43% wt. of oil was obtained as CI seed shell pyrolyzed in the presence of  $\text{Al}_2\text{O}_3$  at the ratio of 8:1. The pyrolytic-oils yielded with and without a catalyst were characterized by FT-IR and GC-MS.

**Keywords**—calophyllum inophyllum seed shell (CI seed shell), Thermal pyrolysis, Catalytic pyrolysis, pyrolytic oil, physical properties, chemical properties

### INTRODUCTION

Energy is the key factor for human development. The standard of living and quality of life extensively depends on energy use in industry, transportation, residential, commercial and agricultural. The world primary energy share about 85%. The world reserve to production ratio of primary energy is very low. The rate of energy consumption is increasing significantly day by day. The world will not be able to sustain so longer based on current reserves of primary energy. Under such circumstance, the world community needs to search new sources of energy which is sustainable and be able to meet the demand. Owing to the rapid increase in the world's industrialization and population, the demand for energy is increasing; some new energy resources are needed to supplement the major conventional energy consumption, such as petroleum, coal and natural gas.

Biomass is one of the most important and potential source of energy. It is available with high carbon content, low ash content, low emission, and low moisture content and it is renewable, inexpensive sustainable feedstock, environmentally friendly and received considerable attention. Biomass is composed of cellulose, hemicelluloses and lignin. It can be transformed into fuels and valuable chemicals within a single facility. Furthermore, in the production of heat and power, the utilization of biomass derivatives mitigates the release of greenhouse gas emissions through cycles of regrowth and combustion.

Among the thermo-chemical conversion processes, four process options are available: pyrolysis, gasification, direct combustion and liquefaction. Pyrolysis is recognized as a promising technology for bio-oil and bio-char. Bio-oils, one of the pyrolysis products, are usually dark brown organic mobile liquids which have a higher heating value than that of the raw material and can be readily stored and transported. It can be used for the production of chemicals and have potential to substitute fuel-oils in many stationary applications for heat or electricity generation. Other challenges for the utilization of pyrolysis oils are that it is acidic, has high water content (15 to 30 wt.%), low H/C ratios and are phase separate when stored. In order to improve the property of bio-oil, chemical processes are required to increase its volatility, thermal stability and reduce viscosity. Literatures disclosed that catalyst with silica and alumina composition and oxides of metal increased the yield and fuel properties by decreasing oxygen content of the pyrolytic oil.

In the present study, thermal pyrolysis and the oxides of aluminum was used as catalyst to study their effect on pyrolysis of CI seed shell. Literatures reported that metal oxide has a significant effect on pyrolysis to increase the physical properties. Aluminum silicates are widely used in catalytic processes, such as the cracking of petroleum fractions, and elucidation of their structures and surface properties. It is an inexpensive catalyst and easily available and hence preferred as a catalyst for pyrolysis. The aim of the study is to improve the fuel properties of pyrolytic oil with the use of catalysts such as  $\text{Al}_2\text{O}_3$  during pyrolysis and to find out the optimum thermal and catalytic condition for maximum yield of pyrolytic oil from CI seed shell.

### EXPERIMENTAL SECTION

**Raw material preparation:** Preparing the raw material to use in the pyrolysis should be done with at most care in order to ensure the quality of the oil obtained. The CI seed was collected from a Punnai tree at coastal area of Nagapattinam. The seed kernel was separated from the shell and shell was allowed to dry for few days in the hot

sun in order to remove moisture content from it. Then the CI seed shell was pulverized into fine grain particles and it was sieved by using various sizes of sievers.

**Characterization of raw material:** The raw material CI seed shell was characterized according to their proximate and ultimate composition analysis. Proximate analysis identified the percentages of moisture, volatile matter, fixed carbon and ash content. The ultimate analysis carried out in CHNSO elemental analyzer to provide the elemental composition. The ultimate analysis identified the percentages of carbon, hydrogen, oxygen, sulphur and nitrogen. The table 1 shows the proximate and ultimate analysis of CI seed shell.

Table 1

	Parameters	Percentage (%)
<b>Proximate Analysis</b>	Moisture	9.56
	Ash	1.75
	Volatile matter	69.04
	Fixed carbon	19.65
<b>Ultimate Analysis</b>	Carbon	76.46
	Hydrogen	6.45
	Oxygen	5.29
	Mineral matter	1.93
	Nitrogen	0.31
	sulphur	Traces

**Thermogravimetric and differential thermogravimetric analyses of raw materials:** Pyrolysis is heating of a substance in absence of oxygen (inert atmosphere) at a particular temperature. Therefore, the temperature for effective pyrolysis of the CI seed shell had to be determined. For this purpose, thermo-gravimetric analysis (TGA) and differential thermogravimetric (DTG) of the sample CI seed shell was done using an instrument NETZSCH STA 449F3. Around 10–20 mg of sample seed was taken and heated in the range of 25°C/10<sup>0</sup>(K/min)/1400°C. The figure 1 shows the Thermo-gravimetric weight loss curve was plotted against temperature.

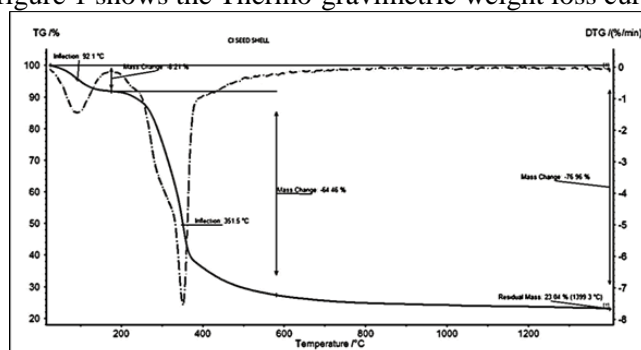


Figure 1

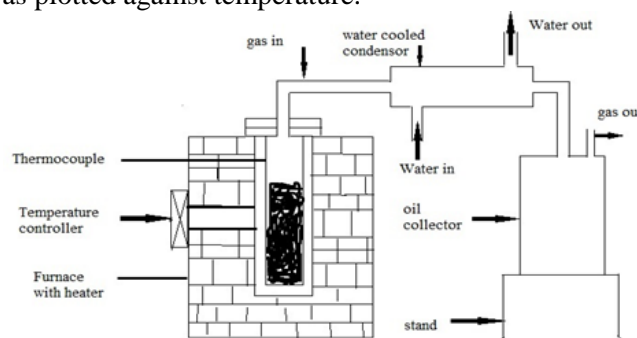


Figure 2: schematic diagram of experimental setup

### Production of Pyrolytic oil

**Experimental Setup:** Figure 2 shows the schematic diagram of the biomass pyrolysis experimental set up. The pyrolysis unit consists of pyrolysis reactor, electrically heated furnace, temperature controller, glass condenser and measuring cylinder. The temperature of the furnace was maintained by highly sensitive PID controller.

The Reactor is made by stainless steel and it consists of thread insulations to prevent the gas from escaping. They are bolted and tightened evenly and properly so as to prevent any leakage of gas which will result in huge loss of potential oil being extracted from the residues inside the reactors. Reactor cap is used to close the bottom side of the reactor. Bio mass is filled up to the reactor cap. Further it provides a gap which is necessary to overcome the effects of thermal stresses which are encountered by the reactor when it is suddenly exposed to larger thermal variation. Temperature controller is used to control the heater. Once the set temperature is reached the temperature controller ensures that the current supply to the heater is stopped.

A condenser is a piece of laboratory glassware used to cool hot vapors or liquids. A condenser usually consists of a large glass tube containing a smaller glass tube running its entire length, within which the hot fluids pass. The ends of the inner glass tube are usually fitted with ground glass joints which are easily fitted with other glassware. During reflux, the upper end is usually left open to the atmosphere or vented through a bubbler or a drying tube to prevent the ingress of water or oxygen. The outer glass tube usually has two hose connections, and a coolant (usually tap water or chilled water/anti-freeze mixture) is passed through it. For maximum efficiency, and to maintain a smooth and correctly directed thermal gradient so as to minimize the risk of thermal shock to adjacent glassware, the coolant usually enters through the lower fitting, and exits through the higher fitting. Maintaining a

correct thermal gradient (i.e. entering coolant at the cooler point) is the critical factor. Normally a high flow rate is not necessary to maintain a cooling surface.

**Feed Material:** CI seed shell of sizes 2.36, 1.18 and 0.7 mm are selected as a feed material for thermal pyrolysis. In the catalytic pyrolysis  $\text{Al}_2\text{O}_3$  was selected as a catalyst to increase the yield and change the properties of pyrolytic-oil.

**Thermal Pyrolysis:** Thermal pyrolysis experiments were conducted in a stainless steel batch reactor with one end opened to collect the volatiles. The reactor was heated electrically by using a cylindrical furnace where PID controller maintained the appropriate temperature with an error of  $\pm 2^\circ\text{C}$ . The reactor was loaded in the range of 60-70 g of CI seed shell sample of different size and inserted vertically into the furnace and pyrolysis experiment was accomplished from 200 to  $400^\circ\text{C}$  at every  $25^\circ\text{C}$  augment of temperature. The generated volatiles were condensed by a water cooled condenser. The condensed liquid was collected using measuring cylinder and measured by weight basis and accordingly the optimum feed size for highest oil yield was determined. At the end of each experiment the reactor was cooled and the solid residue remaining in the reactor was accumulated as char. The % yield of products such as pyrolytic liquid and char was calculated on the basis of their feed. It was observed that the liquid product was easily separated into two layers as per their gravity. The top layer was considered as oil and bottom as aqueous. Hence at each run the weight % yield of oil and aqueous phase was also determined. The percentage of pyrolytic oil is calculated on the basis of feed weight. The following three equations are used to find out the yield of pyrolysis oil, gas and char.

% liquid yield = (liquid weight / feed weight)\*100

% char = (char weight / feed weight)\*100

% flue gas yield = (100-(% liquid yield + % char))

**Catalyst Pyrolysis:** Catalytic pyrolysis experiments were conducted at the optimum feed size and temperature determined by thermal pyrolysis, at different feed to catalyst ratio (6:1, 8:1 and 10:1) in the same stainless steel batch reactor as mentioned in the earlier section. The catalyst  $\text{Al}_2\text{O}_3$  was used directly without any treatment and the yield was calculated as described in the above section. The product obtained from thermal and catalytic pyrolysis was compared on the basis of yield, physical and chemical properties. Later on the process was optimized and the ratio of feed to catalyst for maximum production of pyrolytic oil was determined.

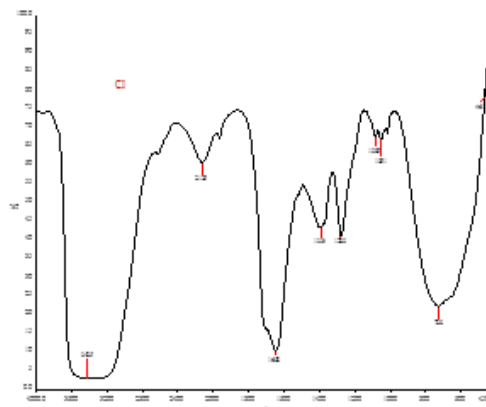
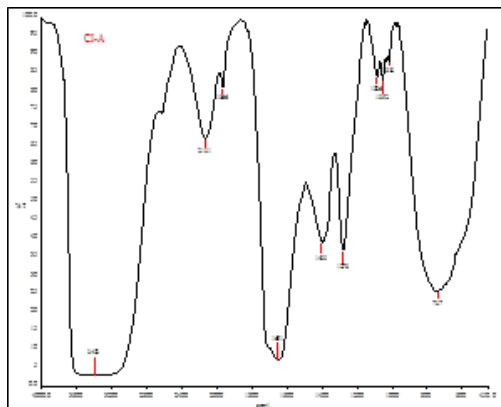
**Characterization of Pyrolytic oil:** The pyrolytic oil was characterized on the basis of their physical properties such as density, viscosity, Flash point, fire point, boiling point, pH value, cetane number, etc. and chemical properties such as functional groups, composition and molecular weight etc.

**Physical properties of pyrolytic oil:** Physical properties were determined for the pyrolytic oil using the American Standards for Testing and Materials (ASTM). Some physical properties of both thermal and catalytic pyrolytic oil were given in table 2.

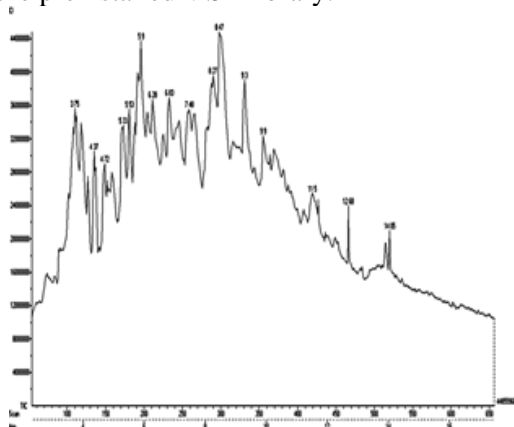
Table.2

Properties	Protocol	Unit	Thermal pyrolysis (CI)	Catalytic pyrolysis (CI-A)
Flash point	ASTM D 92	$^\circ\text{C}$	72	76
Fire point	ASTM D 92	$^\circ\text{C}$	80	82
Calorific value	ASTM D 240	KJ/kg	25141	26321
Density	DM/56	$\text{Kg/m}^3$	1018.33	1020.00
Viscosity at $40^\circ\text{C}$	ASTM D 445	cST	2.71	2.36
PH value	DM/014A	-	3.19	3.59
Cetane number	ASTM D 613	-	43	45
Acid Number	ASTM D 664	KOH/g	7.3	8.1

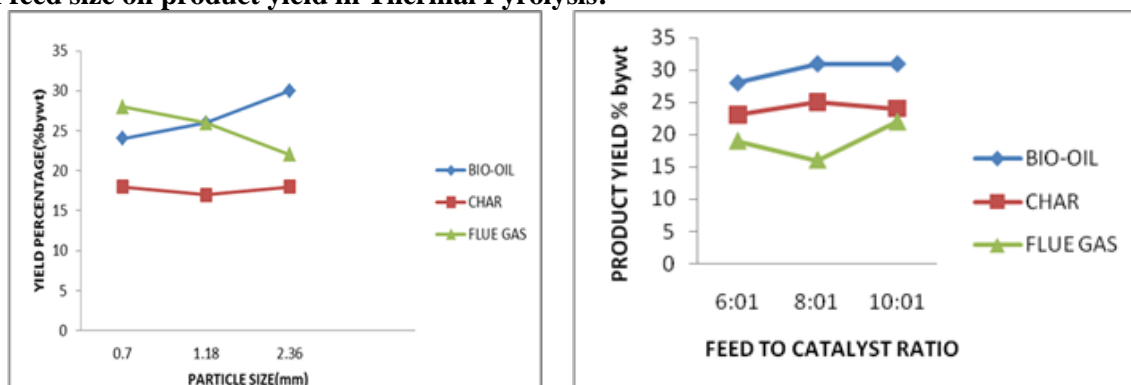
**FTIR (Fourier transforms infrared analysis):** Fourier transform infrared spectroscopy (FTIR) is a technique which provides information regarding functional groups present in the sample. In infrared spectroscopy, IR radiation is passed through a sample. Some of the infrared radiation is absorbed by the sample and some of it is passed through (transmitted). The resulting spectrum represents the molecular absorption and transmission, creating a molecular fingerprint of the sample. Like a fingerprint no two unique molecular structures produce the same infrared spectrum. Perkin Elmer Spectrum1 FT-IR instrument spectrum was collected within the range between  $450$  and  $4000\text{ cm}^{-1}$  at a scan rate of 40 and at a step size of  $4\text{ cm}^{-1}$ . The figure 3 shows FTIR spectra for thermal (CI) and catalytic (CI-A) pyrolysis oil.



**GCMS (Gas chromatography Mass spectrometry):** GCMS is used to find out the chemical compounds present in the sample oil. GCMS is an analytical method that combines the features of gas-liquid chromatography and mass spectrometry to identify different substances within a test sample. The GC separates chemicals based on their volatility, or ease with which they evaporate into a gas. The MS is used to identify chemicals based on their structure. The JEOL GCMATE II GC-MS with Data system is a high resolution, double focusing instrument was used. The GC chromatogram was collected at different retention time and the respective mass spectra were identified from the preinstalled NIST library.



### Effect of feed size on product yield in Thermal Pyrolysis:



The effect of feed size on percentage of product yields in thermal pyrolysis is shown in figure 5. It was observed that the percentage yield of liquid product was maximum 43wt% of total biomass yield of size 2.36mm. The liquid product increases with increase in feed size and peaked 43%wt at feed size 2.36 and a downward trend is observed of feed size beyond 2.36. In contrast the gas production with increasing feed size shows opposite in nature to liquid product. Smaller feed size provides more reaction surface causes high heating rate and too quick decomposition of crushed CI seed shell. The product oil vapors comparatively get enough time for secondary reaction in the reactor and consequently increase in gas yield and decrease in liquid and char yields. On the other hand, the heating rate in larger feed is low due to its lower thermal conductivity and heat can flow only to a certain depth in the available pyrolysis time compared to almost complete thermal decomposition of the smaller particles. Thus the feed of larger pieces becomes carbonized and/or cannot be decomposed completely resulting increase in char yield and decrease in liquid and gas yields.

**Effect of feed to catalyst ratio on product yield in Catalytic Pyrolysis:** Catalytic pyrolysis of CI seed shell was carried out at three different feed to catalyst ratio such as 6:1, 8:1, 10:1. Figure6 demonstrates the effect of catalyst  $\text{Al}_2\text{O}_3$  on the yield of liquid at various feed to catalyst ratio. Since the main objective of the work was to produce liquid fuel, hence, the focus was only on the yield of pyrolytic oil. The comparison between thermal and catalytic pyrolysis confirmed that catalyst had an effect on the yield of liquid. The yield of total liquid was higher at 8:1 feed to catalytic ratio. However, the yield of pyrolytic oil was maximum for catalyst ( $\text{Al}_2\text{O}_3$ ) at 8:1 CI seed shell to alumina ratio, there will be less flue gas yield at 8:1. Hence ratio 8:1 is considered as optimum ratio for this process. The comparison between thermal and catalytic pyrolysis confirmed that catalyst had an effect on the yield of liquid. The yield was marginally higher (up to 5%) for  $\text{Al}_2\text{O}_3$  catalytic pyrolysis at 8:1 feed to catalyst ratio than thermal pyrolysis.

**Effect of catalyst on physical properties of pyrolytic oil:** Table 2 represents the physical properties of the thermal and catalytic pyrolytic oil produced at the optimum condition. The physical properties such as density, viscosity, pH, calorific value were evaluated and compared. The decrease in viscosity of oil was observed in catalyst pyrolysis over thermal pyrolysis. Catalyst pyrolysis with  $\text{Al}_2\text{O}_3$  at 8:1 ratio produced less viscous (2.36 cST) pyrolytic oil than other thermal pyrolysis. A variation in calorific value of the catalytic pyrolytic oil was noticed. The calorific value of thermal pyrolytic oil was found to be 25141 KJ/ kg. It was observed that the calorific value increased with catalyst pyrolysis with  $\text{Al}_2\text{O}_3$  (26321 KJ/ kg) in comparison with thermal pyrolysis. The positive impact of catalyst pyrolysis on pH was also observed. The catalyst was competent to increase the pH resulting in less acidic oil, altering the pH from 3.19 to 3.59. From Table 2, it can be seen that the Flash point, Fire point and Cetane number of the catalytic pyrolytic oil increased slightly in comparison with thermal pyrolytic oil. In general, oxygen content of thermal pyrolytic oil is higher which decreases the stability as well as the calorific value. The other factor that also affects the thermal stability is the pH of the oil. Lower pH increases the acidity of the pyrolytic oil which is thus not suitable as fuel for diesel engine. The major drawback of pyrolytic oil is higher viscosity which creates a problem during the atomization in a diesel engine. All these physical properties are related to each other. This can be overcome by catalyst pyrolysis. During catalyst pyrolysis, the oxygen is removed from pyrolysis vapor with the formation of  $\text{CO}_2$ ,  $\text{CO}$  and  $\text{H}_2\text{O}$ . This results in increase in calorific value of pyrolytic oil. The formation of water decreases the viscosity of pyrolytic oil. Water reduces the viscosity and enhances the fluidity, which is good for the atomization and combustion of pyrolytic oil in the engine.

**FTIR analysis of pyrolytic oil:** The FT-IR results from the transmittance spectrums are presented in Table 3. The chemical structures of pyrolytic-oil and sub fractions are made up of a large number of atomic groupings and structures. Very similar FTIR spectra were obtained for CI seed shell thermal and 8:1  $\text{Al}_2\text{O}_3$ . The band intensities reveal that the most abundant chemical bonds in bio-oil and sub fractions are O-H, C-H, C=O, C-C and C-O. The data shows that the present liquid contains mainly alcohol, alkynes, alkanes, aromatic and phenolic compounds. Broad O-H stretching vibrations in the range of  $3600\text{--}3200\text{ cm}^{-1}$  indicate the presence of alcoholic and Phenolic compounds in the pyrolytic oil. The presence of terminal alkenes is indicated  $\text{C} \equiv \text{C}$  deformation vibrations at  $2100$  and  $2140\text{ cm}^{-1}$ . The presences of dienes are indicated C-C stretching vibrations at strong absorptions of  $1650\text{ cm}^{-1}$ . The peaks between  $1100$  and  $1000\text{ cm}^{-1}$  are suggested fluoroalkanes. The presence of aromatics groups are indicated C-H stretching vibrations at strong absorptions of  $745\text{ cm}^{-1}$ . Several literatures have given the similar FT-IR results of different biomass pyrolytic oil which is being used as fuel FT-IR fractional groups and the indicated compounds of the pyrolysis oil.

**Table.3.**

Functional groups with respect to wave number present in pyrolytic oil		
Frequency range ( $\text{cm}^{-1}$ )	Bond	Class of compound
3600-3200	O-H	Alcohols and phenol
2100-2140	$\text{C} \equiv \text{C}$	terminal alkynes
1650	C-C	dienes
1395	C-H	Alkyl
1278	C-O	carboxylic acids
1100-1000	C-X	fluoroalkanes
745	C-H	Aromatic

**GC-MS analysis of pyrolytic oil:** The results of physical properties confirmed that catalyst pyrolysis of CI seed shell with  $\text{Al}_2\text{O}_3$  in the ratio of 8:1 offered good quality of oil compared to thermal pyrolytic oil. The composition of both thermal and catalytic pyrolytic oil were determined by GC-MS analysis and presented in Table 4. Pyrolytic oil is a complex mixture of several oxygenated compounds. These compounds involve methyl, phenol, acids, esters, hexane, benzene, amine and other alkane compounds. The effect of catalyst on thermal pyrolysis was observed and discussed. It was observed that similar kinds of compounds were present in thermal and catalytic pyrolytic oil with a little variation. Allylcyclopropane carboxylic acid, Heptadecanoic acid and Tetradecenoic acid were present in thermal pyrolytic oil whereas Pentadecanoic acid and Heptadecanoic acid were present in catalyst pyrolytic oil. The GC-MS analysis confirmed that CI seed shell catalyst pyrolytic oil contains a maximum amount of methyl group compounds with a lower amount of benzene, acids and other compounds.

## CONCLUSION

Thermal and catalytic pyrolysis of CI seed shell was carried out and the resultant oils were characterized for their physical and chemical properties. From thermo-gravimetric analysis (TGA) the rapid decomposition of CI seed shell occurred between temperatures  $250$  to  $400^\circ\text{C}$  with  $64.46\%$  weight loss. So the slow pyrolysis process type was carried out. In thermal pyrolysis feed size of  $2.36\text{ mm}$  gives the maximum yield of the pyrolytic liquid. Catalyst pyrolysis  $\text{Al}_2\text{O}_3$  used as catalyst and effect of  $\text{Al}_2\text{O}_3$  on pyrolysis was evident from the fact that this catalyst marginally increased the yield of pyrolytic liquid in comparison with thermal pyrolysis. The yield of catalytic pyrolytic oil was maximum  $43\text{ wt}\%$  for  $\text{Al}_2\text{O}_3$  at the ratio of 8:1. Hence, 8:1 feed to catalyst ratio was accepted as the optimum condition for maximum yield of pyrolytic oil from CI seed shell. The pyrolytic oil both thermal and catalyst was characterized by its physical and chemical properties. In both pyrolysis functional groups present in the pyrolytic oil were alcohols, phenol, terminal alkynes, dienes, alkyl, carboxylic acids, fluoroalkanes and aromatic. The GCMS report confirms functional group presented in pyrolytic oil. The comparison between thermal and catalytic pyrolysis confirmed that catalyst had a little effect on the yield of pyrolytic oil. However, the catalyst resulted in better oil quality in terms of enhanced calorific value, reduced viscosity and changed pH.

From this study it was concluded that CI seed shell can be used as a suitable feed stock for pyrolysis and the pyrolytic oil can be used as fuel oil. The catalytic pyrolysis of CI seed shell confirmed that the presence of catalyst increased the fuel quality, however the fuel properties were changed little amount only. In this work only  $\text{Al}_2\text{O}_3$  was used as catalyst, however more study using different catalysts need to be done to find out the best catalyst which will improve the fuel quality with better properties.

Table.4

Retention time	Compound Name	Peak area (%)
<b>Composition of Thermal Pyrolytic oil (CI)</b>		
3.75	Cyclopentanethiol,2-methyl-,trans	7.12
4.37	2-Pyrroline,1,2-dimethyl	2.73
4.72	Spiro[2.4]heptan-4-one	4.07
5.33	1H-Imidazole,2,4,5-trimethyl	8.57
5.53	2-Methyl-1-ethylpyrrolidine	15.09
5.93	Bicyclo[[2.2.2]octan-1-amine	5.98
6.28	1-Allylcyclopropanecarboxylic acid	2.99
6.83	1,4-Benzenediol,2,5-dimethyl	7.61
7.48	2-[1,5-dimethyl-hexyl]-cyclobutanone	3.30
8.27	6-Hydroxymethylbicyclo[2.2.1]heptan-2-one	11.58
8.47	Benzenemethanol,3-hydroxy-5-methoxy	11.58
9.35	3,6-Diazahomoadamantan-9-ol	7.73
9.92	3a,6,6-Trimethyl-hexahydro-benzofuran-2-one	2.80
11.5	Bicyclo[4.3.0]nonan-7-one,1-[2-methoxyvinyl]	4.27
12.68	E-9-Tetradecenoic acid	1.53
14.05	Heptadecanoic acid,9-methyl-,methyl ester	3.05
<b>Composition of Catalyst Pyrolytic oil (CI-A)</b>		
3.85	Cyclohexanol,3-methyl	6.11
4.45	1,3-Cyclohexanediol,cis	1.35
5.38	Cyclohexanone-,2-[hydroxymethyl]	3.97
5.75	2-Methyl-7-norbornanol	4.06
6.1	3-Cyclohexen-1-carboxaldehyde,3-methyl	2.04
6.75	3-Cyclohexen-1-carboxaldehyde,3,4-dimethyl	46.90
6.78	2-Oxatricyclo[4.3.1.0[3,8]]decane	4.30
7.17	2-Hydroxy-6-methyl-3-cyclohexen-1-carboxylic acid	2.85
7.62	2-Isopropylidene-5-methylhex-4-enal	5.68
8.22	4-Hydroxy-3-pentyl-3-cyclohexanone	3.93
8.48	Benzenemethanol,3-hydroxy-5-methoxy	6.70
9.3	Phenol,4-methoxy-3-[methoxymethyl]	5.31
9.87	3a,6,6-Trimethyl-hexahydro-benzofuran-2-one	0.70
11.5	Bicyclo[4.3.0]nonan-7-one,1-[2-methoxyvinyl]	3.22
12.68	Pentadecanoic acid,13-methyl-,methyl ester	1.23
13.23	Estra-1,3,5[10]-trien-17-a-ol	1.64
14.02	Heptadecanoic acid,9-methyl-,methyl ester	2.39

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