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Studies on Catalytic Pyrolysis of Mustard Press Cake with NaCl

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Abstract

Under this present investigation, non-catalytic and catalytic pyrolysis of mustard press cake (MPC) was conducted in a 50 mm diameter and 640 mm long semi-batch pyrolyser in the temperature range of 673K to 1173K in a nitrogen atmosphere. Effects of temperature on yields of products, namely, char, pyro-oil and gas obtained from primary pyrolysis of MPC have been investigated. The kinetic rate constants of volatiles and char formations were determined in the temperature range under the study. The activation energies and pre-exponential factors were determined. The catalytic effects of NaCl on the pyrolysis of MPC have also been investigated at three different temperatures namely, 673K, 773K and 873K. Catalyst loading was varied from 5-15% (w/w biomass). The product yields of catalytic and non-catalytic pyrolysis of MPC was compared. The activation energies of catalytic pyrolysis have been observed to be low in comparison to non-catalytic ones.

Keywords: Mustard press cake, Catalytic and Non-catalytic pyrolysis, NaCl catalyst, Reaction kinetic, Product yield

Introduction

In current business scenario, conventional fossil fuels as energy resources will be extinct within 40-50 years due to the abruptly increasing price of crude oil and fluctuating economic growth rate of India. On the other hand, greenhouse gases mainly, CO_2, contribute to the global climate changes. But due to the rapid growth of population the demand of energy is continuously increasing in India. Therefore, the recovery of energy from renewable sources is necessary. Nowadays biomass is considered as major renewable sources to produce the potential energy in near future. Since biomass contains negligible amount of sulphur, nitrogen and metal content, the energy generated through biomass also reduces the emission of CO_2 and SO_2[1]. Generation of biofuel from biomass may be through chemical, biochemical and thermochemical processes. Among several thermochemical conversion processes such as, pyrolysis, combustion and gasification, pyrolysis method has been introduced as most recent renewable energy process for producing (1) char, which might be used as solid smokeless fuels for barbeque, activated carbon and an adsorbent or for landfilling, (2) pyro-oil, which might be used as a fuel, an energy carrier and a source of chemical and (3) the gaseous product might be used for all energy requirements of the pyrolysis plant due to its higher calorific value. The production of char, pyro-oil and gas might be maximized just by the adjustment of pyrolysis technique and reaction parameters.

The quality and composition of the pyro-oil depends on the biomass composition and its extractive content. Therefore, higher yield of pyro-oil may be obtained during pyrolysis of the agricultural residues (biomass) due to its higher amount of extractives and cellulose. Several research works have already been reported regarding various aspects of pyrolysis of agricultural residues namely, sesame, mustard and neem de-oiled cake[2], jatropha oil cake[3], olive residue[4], rapeseed cake[5, 6], pungam oil cake[7], sunflower oil cake[8], safflower oil cake[9], cotton seed cake[10], soyabean cake[11] and mustard press cake[12] etc. The pyro-oil obtained from biomass could not be used directly due to its high viscosity, corrosiveness, poor heating value and relative instability. Therefore, a upgrading process is required for removal of oxygen content of the pyro-oil[13, 14]. Several methods have already been examined for upgrading the pyro-oil quality, namely, catalytic cracking of pyrolysis vapors, hydrodeoxygenation, extracting chemicals, and esterification etc. In recent year among these methods the catalytic pyrolysis of biomass has been receiving great attention due to its significant processing

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and economic advantage over hydro-treating in absence of H_2[15]. Catalytic pyrolysis of various type of oil cake namely, rapeseed cake[16-18], karanja seed[19], mohua seed cake[20], sunflower oil cake[21] and sufflower oil cake[22] have already been reported. However, no works have been reported on the catalytic pyrolysis of mustard press cake.

Under this present investigation, mustard press cake (MPC) has been selected as a pyrolysis feed stock. Catalytic and non-catalytic pyrolysis of MPC was conducted in a packed bed reactor. Effects of temperature on yields of products obtained from catalytic and non-catalytic pyrolysis of MPC has been investigated. The activation energies and pre-exponential factors of catalytic and non-catalytic pyrolysis have been determined.

Materials and methods

Materials

Mustard press cake (MPC) sample has been collected from a local oil mill situated near Jadavpur University, Kolkata. The proximate and ultimate analyses of mustard press cake have been listed in table 1. The ultimate analyses have been done using CHNSO analyser (2400 series-II, Perkin Elmer, U. S. A.). Calorific value of raw materials has also been determined using bomb calorimeter, i.e. 14.56 MJ/Kg.

Table 1. Proximate and ultimate analyses of feed stock

Property	Wt %
Moisture content	14.34
Volatile matter	63.49
Ash content	7.7
Fixed carbon	14.47
C	40.26
H	6.03
N	6.46
S	1.11
O	46.14

Experimental

Non-catalytic Pyrolysis

The non-catalytic pyrolysis experiment of MPC was conducted in a 50 mm diameter and 640 mm long cylindrical stainless steel fixed bed pyrolyser in the temperature range of 673K to 1173K. The experimental procedure has already been discussed in previous study done by Chowdhury et al.,[23] and Sarkar et al.,[12].

Catalytic Pyrolysis

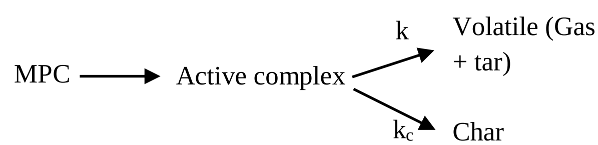
The MPC was impregnated with NaCl (Merck purity >99 %) by quenching of the MPC with the NaCl solution and by subsequent, evaporation of the moisture in the hot air oven. The catalytic pyrolysis of MPC was carried out in the same pyrolyser[23, 12] at temperatures of 673K, 773K and 873K with 5 % NaCl, (w/w). Catalyst loading was varied from 5-15% (w/w MPC).

Pyrolysis kinetics

Pyrolysis of MPC sample proceeds through complex reactions in series, parallel or combination of both. Under the present study a parallel reaction model has been attempted to describe pyrolysis kinetics of MPC. The reaction kinetics of volatile and char have been elaborately discussed in pyrolysis of coconut shell[24], vegetable market waste[25] and textile wastes[23]. The reaction pathway of pyrolysis according to the present model is as follows,

Results and Discussion

Effect of pyrolysis temperatures on product yield



After completion of catalytic and non-catalytic pyrolysis of mustard press cake, the solid residue was collected from the reactor. From the kinetic model[24, 25], the amount of unreacted sample and the char yield were determined. The condensable part of volatile was considered as pyro-oil. The gas yield was calculated by subtracting the amount of pyro-oil from the yield of volatiles.

Non-catalytic pyro-product yield

The yields of char, pyro - oil and gases obtained from non-catalytic pyrolysis of MPC in relation to the process conditions are shown in figure 1.

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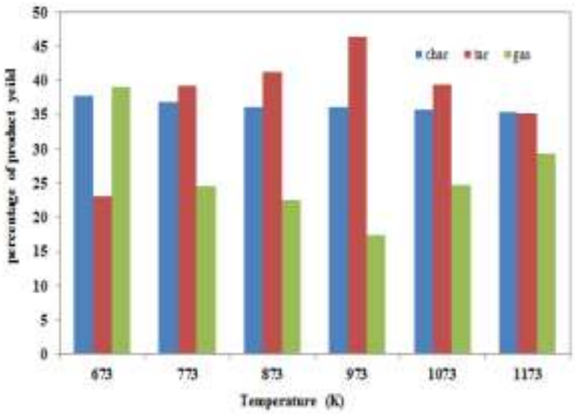

Figure 1. Percentage of product yields obtained at one hour from non-catalytic pyrolysis of mustard press cake (MPC) at different temperatures

The char yield decreased from 37 – 35% when the temperature was increased from 673 to 1173K. The decrease in the char yield with pyrolysis temperature is to be attributed to an increasing de-volatilization of the solid hydrocarbons in the char. Partial gasification of the carbonaceous residue is also possible[26].

On the other hand, the bio-oil yield increased from 39 to 46 % when the temperature was increased from 673K to 973K. Above this temperature, the yield of bio-oil decreased. In case of castor seed[27], mustard cake[2], polanga seed cake[28] similar trend of bio-oil have been reported. At 1173K the yield of bio-oil was 35%. Appearance of a maximum in the trend of yield of pyro – oil against temperature may be due to the commencement of further cracking of tar molecules to lower gaseous molecules at higher temperatures.

The gas yield obtained from MPC gradually decreased from 39 – 18% respectively with the rise of temperature from 673K to 973K. Above this temperature the gas yield suddenly increased from 22% to 29% with the rise of temperature from 1073K to 1173K. The increase in gaseous products may be due to the secondary cracking of the pyrolysis vapours at higher temperature. Nevertheless, as already mentioned, the secondary decomposition of the char at high temperatures may also give non-condensable gaseous products, owing to a heterogeneous reaction between the char and gaseous components such as H_2O[26].

Catalytic pyro-product yield

Char yield

The char yield obtained by the non-catalytic and catalytic pyrolysis of MPC has been shown in figure 2.

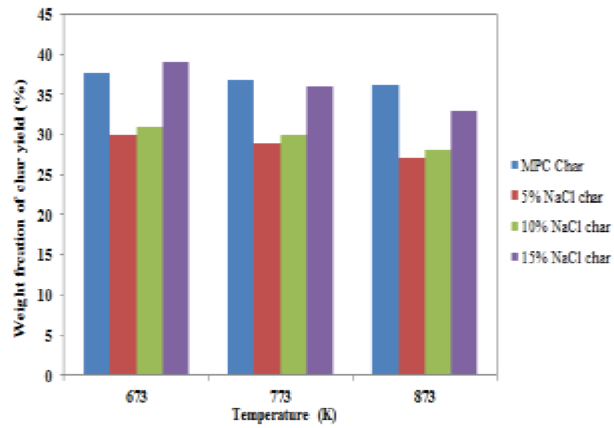

Figure 2. Distribution of weight fraction of char yield at different temperature and at different concentration of NaCl

It can be seen that char yield decreased with the rise in pyrolysis temperature. From the close observation of the data it also appears that the catalyst has significant effect on char yield. The yield of char increased significantly with the addition of catalyst at various concentrations.

In case of non-catalytic pyrolysis, the char yield decreased from 37.72 – 36.21% when the temperature was increased from 673 to 773K. In case of catalytic pyrolysis at 773K the amount of char yield were 27%, 28% and 33% at different concentrations of NaCl, namely, 5%, 10% and 15% respectively. This decrease in char yield during the studies of catalytic pyrolysis of MPC was related to the higher ratio of heat carrier to biomass resulting in higher volatilization rate of biomass particles[29]. Similar trend has been observed by previous researchers during the studies of hydrothermal treatment of biomass[30] and catalytic pyrolysis of woody biomass[31].

Pyro-oil yield

The yields of pyro-oil obtained from non-catalytic and catalytic pyrolysis of MPC at three different temperatures and at three different concentrations of NaCl have been shown in figure 3.

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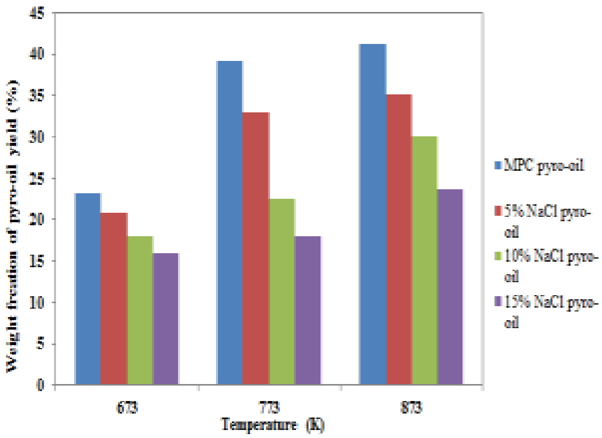

Figure 3. Distribution of weight fraction of pyro-oil yield at different temperature and at different concentration of NaCl

During the studies of non-catalytic pyrolysis, the maximum pyro-oil yield of 41.17% was obtained at 873K. In presence of catalysts, decrease of tar yield of 6%, 11% and 18% in comparison to non-catalytic pyrolysis has been observed at 873K when the loading of NaCl is maintained at 5%, 10% and 15% respectively. This may be due to the increase of secondary tar cracking reactions under the influence of catalysts.

Gas yield

The distribution of gaseous product at different non-catalytic and catalytic temperatures and at different concentrations of NaCl has been shown in figure 4.

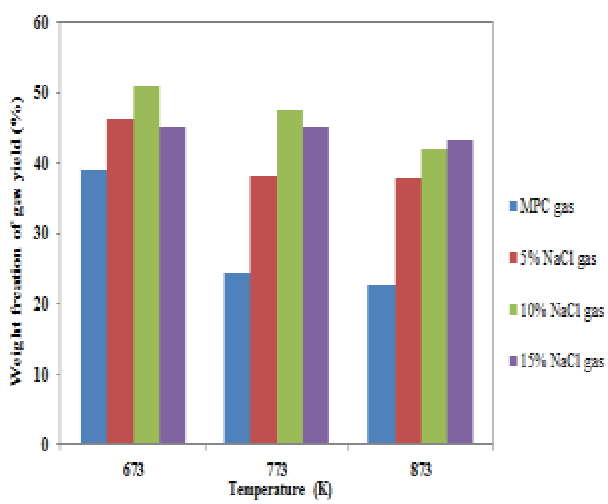

Figure 4. Distribution of weight fraction of gas yield at different temperature and at different concentration of NaCl

The percentage of gas yield decreased with the rise of temperature in case of non-catalytic pyrolysis of mustard oil cake. However, the gas yield becomes higher when catalyst is used. The justification is probably the same as in case of decrease of tar yield of catalytic pyrolysis in comparison to non-catalytic pyrolysis, i.e., due to the increase in the rate of secondary tar cracking reactions.

Activation energy and frequency factor

The values of frequency factors and activation energies of the reactions of reactant decomposition, volatile formation and char formation are determined by regression analysis of the rate constant of non-catalytic pyrolysis of MPC determined in the temperature range of 673K to 1173K[24, 25]. The frequency factors and activation energies of different reactions of catalytic pyrolysis of MPC has also been determined in the temperature range of 673K to 873K. All values have been mentioned in table 2.

Table 2 Calculated Activation Energies and Frequency Factors as per Arrhenius Law

Reaction rate constant	Activation energy (KJ/mol)			Frequency factor (min^{-1})			Correlation coefficient
	MPC	5% NaCl	15% NaCl	MPC	5% NaCl	15% NaCl	
k	16.15	9.12	7.37	0.263	1.19	2.73	1.0
k_v	16.47	11.26	9.64	0.175	1.21	3.01	1.0
k_c	15.47	4.21	3.35	0.087	8.73	14.21	1.0

From the analysis of the table, it is evident that the activation energy and frequency factor decreases and increases respectively with the increase of catalyst loading. This clearly indicates the positive influence of NaCl catalyst on pyrolysis rate of MPC in the entire temperature range under study.

Conclusion

In this present study, the mustard press cake was chosen as a pyrolysis feed stock to produce pyro-oil and char. The effect of temperature (673K to

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873K) on product yields has been studied. This parameter has shown significant influence on pyrolysis product yields. The kinetic rate constants of reactions responsible for volatile and char formation were determined in the temperature range under the study. The activation energies and pre-exponential factors were determined. Catalytic pyrolysis of MPC was carried out at three different temperatures namely, 673K, 773K, 873K and at three different concentrations of NaCl (5-15%). The product yields obtained from MPC through catalytic and non-catalytic pyrolysis were compared. While the yields of char and pyro-oil obtained during the catalytic pyrolysis are lower than the non-catalytic pyrolysis, the gas yield shows the opposite trend, i.e., higher yield of gas is observed in presence of catalysts. The activation energies of catalytic pyrolysis have been observed to be low in comparison to non-catalytic ones, signifying the overall increase of rate of pyrolysis in presence of NaCl. Thus, NaCl may be successfully utilized for the enhancement of pyrolysis rate of MPC. Catalytic effect of NaCl is also expected in case of pyrolysis of other similar feed stocks.

Acknowledgements

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