Kinetics and Thermodynamics of Oil Extraction from Jatropha Curcas in Aqueous Acidic Hexane Solutions

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Abstract: Jatropha oil curcas (JOC) extraction was performed in aqueous HCl, H_2SO_4, and H_3PO_4 solutions with n–hexane (C_6H_{14}) at 30, 40, 50, and 60 °C using 10 gm of Jatropha seeds over 1 hours with 10 minutes sampling intervals. The optimum acid concentration was 15 % by weight for each acid, and the highest oil yield was obtained in the extraction procedure with n–hexane containing HCl. The extraction process was observed with regard to the percent oil yield versus time, and the reaction order was found to be first–order kinetics by the differential method. The activation energy for the oil extraction kinetics of Jatropha seeds with 15 % HCl was Ea = 26.6763 kJ/mol, and the activation thermodynamic parameters at 60 °C were $\Delta H^{\neq}$ = 23.908 kJ/mol, $\Delta S^{\neq}$ = – 239.927 J/mol.K, and $\Delta G^{\neq}$ = 103.803 kJ/mol. The enthalpy value was ΔH = 0.1586 kJ/mol, and the other thermodynamic parameters at 60 °C were calculated to be ΔS = 15.275 J/mol.K, and ΔG = – 4.928 kJ/mol. [Journal of American Science. 2010;6(11):293-300]. (ISSN: 1545-1003).

Key words: kinetics, thermodynamics, oil extraction, Jatropha curcas.

1. Introduction

Jatropha is a genus of over 170 plants from the Euphorbiaceae family, native to the Central America but commonly found and utilized across most of the tropical and subtropical regions of the world. It has a yield per hectare of more than four times that of soybean and ten times that of corn (1). Jatropha curcas is a wonder plant with a variety of applications and enormous economic potentials (2).

Extracts from this species have been shown to have anti–tumor activity (3), the leaves can be used as a remedy for malaria and high fever (4, 5), the seeds can be used in treatment of constipation and the sap was found effective in accelerating wound healing procedure (4). Moreover, this plant can be used as an ornamental plant, raw material for dye, potential feed stock, pesticide, soil enrichment manure and more importantly as an alternative for biodiesel production (6, 7).

Oilseeds are extracted in two ways, by squeezing or mechanical pressing and with chemical solvents. Prior to the 1940's, mechanical pressing was the primary method used, but it had its limits in terms of oil recovery. By mechanical pressing, only 5–6 % of the oil was difficult to achieve (8), and also pressing generates high temperatures which damage both oil and meal (8).

Solid liquid extraction is a common and efficient technique in producing oil for biodiesel production. Solid liquid extraction, sometimes called leaching, involves the transfer of a soluble fraction (the solute or leachant) from a solid material to a liquid solvent (9). Solvent extraction was developed because it allows more complete extraction at lower temperatures. Extraction using supercritical fluid (10), the oil produced has very high purity; however the operating and investment cost is high (10). Solvent extraction has several advantages, it gives higher yield and less turbid oil than mechanical extraction, and relative low operating cost compared with supercritical fluid extraction (11). For many years, commercial grade hexane was been the solvent of choice for the extraction of oil from oilseeds. Alternative hydrocarbon solvents for cottonseed extraction was recommended (12), heptane and iso–hexane as potential replacements for hexane.

In the present investigation, oil extraction from Jatropha seeds in aqueous hydrochloric acid (HCl), sulfuric acid (H_2SO_4) and ortho–phosphoric acid (H_3PO_4) solution with n–hexane (C_6H_{14}) was studied. The aim of the study was to find the optimum acid concentration and most effective acid from HCl, H_2SO_4 and H_3PO_4, and, in physicochemical terms, to determine the kinetic and thermodynamic parameters of oil extraction from Jatropha seeds.

2. Materials and Experimental

2.1. Materials used:

2.1.1 Jatropha seeds:

Jatropha seeds were purchased from local market "Ministry of Agriculture". For the extraction process, the seeds were shelled, and then ground to a mesh size of 40 (425 µm). The moisture content of the ground Jatropha seeds was 7.48 %.

2.1.2 Solvent acid solutions:

The normal hexane (C_6H_{14}), hydrochloric acid (HCl), sulfuric acid (H_2SO_4), and ortho–phosphoric acid (H_3PO_4), were used to prepare aqueous acid solution as wt. 0 % (without acid only hexane with distilled water), 5 %, 10 %, 15 %, 20 %, 25 %, and 30 %.

2.2. Experimental Set–Up:

Figure (1) illustrates a schematic diagram of a bench scale extraction set–up which consists mainly of a three necked flask (250 mL) with a round bottom. The large neck in the middle of the flask was connected to a reflux condenser, a thermometer was placed in one of the two side necks, and the third neck was used for taken samples during the extraction process period. The flask was submerged in a temperature controlled water bath with magnetic stirrer.

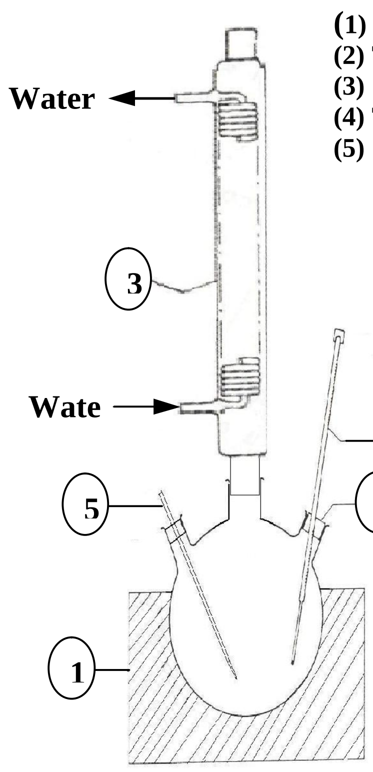

Fig. (1): Bench Scale Extraction Set–Up

2.3. Procedure and Experimental Conditions:

2.3.1. Laboratory Scale:

Ground Jatropha seeds (10 gm) was put in a three–necked flask (250 mL) with a round bottom containing 76 ml of hexane and 76 ml of acid solution (for each acid solution), and the following temperatures were used 30, 40, 50, and 60 °C. The total extraction time was 60 minutes. Miscella batch samples were collected in reweighed beakers at time intervals 10 minutes of extraction. The amount of oil extracted in each time interval was determined gravimetrically by measuring the weight of the residue after filtration and drying by recovering solvent.

2.3.2. Bench Scale:

100 gm of ground Jatropha seeds were extracted using 760 ml of hexane and 760 ml of acid solution at 60 ºC for 3 hours. Miscella obtained after filtration was collected in a separating funnel in which the upper clear layer is a mixture of oil and solvent. The amount of oil extracted was determined gravimetrically by weighing the oil after drying for solvent recovery.

3. Results and Discussion

3.1 Laboratory Scale Results:

3.1.1 Effect of Acid's Types and Concentrations:

The percent oil yield values for the different acid solutions at 60 °C and 60 min time extraction are shown in figure (2) for oil extraction from Jatropha seeds. As seen in figure (2), the oil yields peaked (optimum value) at the 15 % concentration for each acid and decreased inversely to acid concentration after this optimum value. At this optimum acid value, it decreased the hexane penetration path lengths and resulted in an increase in the amount of oil extracted [(13)].

Since the highest oil yield was obtained with HCl over H_3PO_4 and H_2SO_4, then the most effective acid was HCl. The kinetic and thermodynamic parameters were calculated according to the values at a 15 % acid concentration. The percent oil yields for 15 % HCl at various temperatures are given in table (1) for Jatropha seed oil extraction.

From these results, it is obvious that maximum oil extracted reached 24.216 % of seeds at 60 °C, (i.e) the extracted oil is 85.569 % from the available oil which is 28.3 %, because the oil source was Jatropha trees only of two years old [(14)].

Table (1): Percent of JOC at various extraction temperatures for 15 % HCl containing n–hexane

Time , min	Oil Yield (%), Y 30	40	50	60
10	12.578	14.211	16.112	16.948
20	13.263	15.148	17.201	18.201
30	13.976	16.113	18.438	19.552
40	14.782	17.145	19.713	21.048
50	15.578	18.321	21.172	22.536
60	16.481	19.518	22.602	24.216

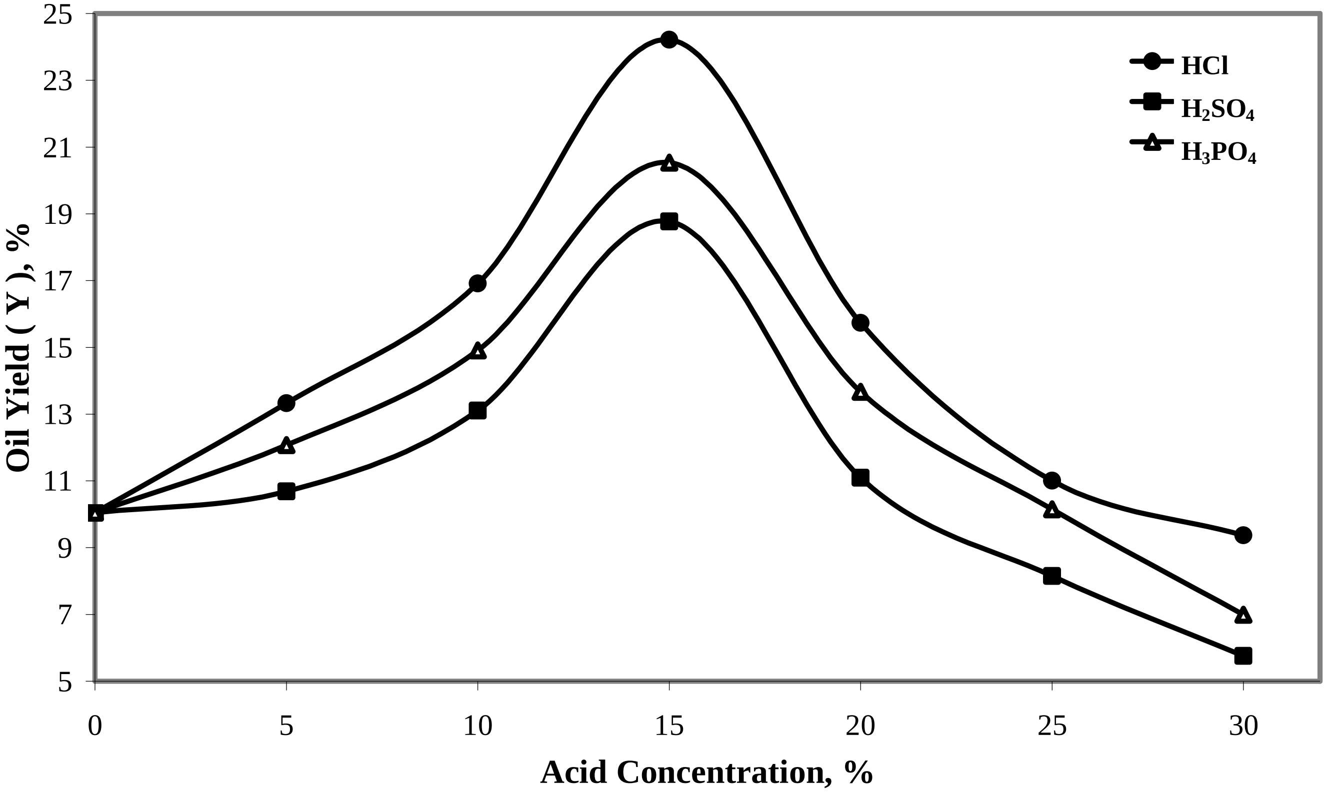

Fig. (2): Effect of Acid Concentration on Percent JOC (Y) at 60 °C and 60 min

3.1.2 Extraction Kinetics:

A reaction rate equation for oil extraction from Jatropha seeds can be written as [13, 15]:

$$\frac{dY}{dt} = kY^{n} \qquad (1)$$

where Y is the percent oil yield, t is the time of extraction (min), k is the extraction constant, and n is the reaction order. Since the percent oil yield increased in the course of time, the terms dY/dt have a positive sign [13].

Using the values in table (1) and applying the Differential Method, plots of ln (dY/dt) versus ln Y for 15 % HCl were drawn and were found to be linear according to equation (1). A first–order kinetics was found from the values of n obtained, with average R^2 = 0.93, from the slopes of the straight lines in figure (3), and the reaction rate constants were calculated from the slopes (Table 2).

Table (2): Values of the reaction rate constants for JOC extraction with 15 % HCl containing n–hexane at various temperatures

T (^oC)	k (min^{-1})
30	$2.8744*10^{-3}$
40	$4.834*10^{-3}$
50	$5.7878*10^{-3}$
60	$7.781*10^{-3}$

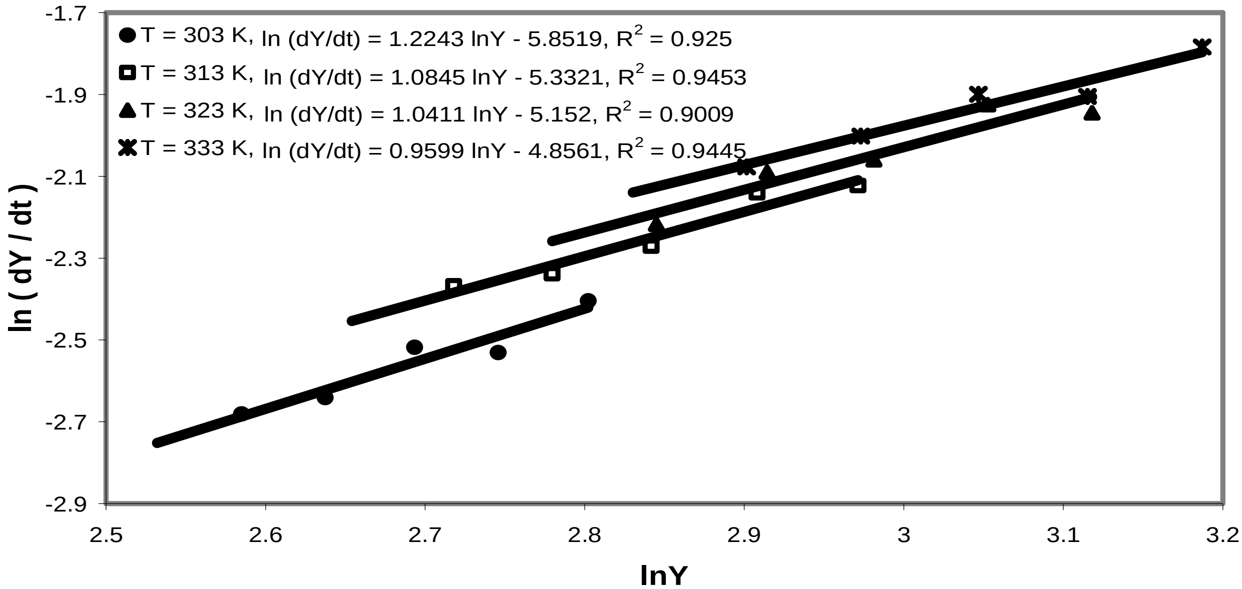

Fig. (3): A Plot of [ln (dY/dt)] versus [ln Y] at Different Temperatures for JOC Extraction with 15 % HCl Containing n–Hexane

3.1.3 Calculation of Activation Energy:

The rate constant k increases with increasing temperature, and this trend is obvious in table (2). The changes can be described by the Arrhenius Equation [2, 13, 15]:

$$k = Ae^{-Ea/RT} \qquad (2)$$

where k is the reaction rate constant, A is the Arrhenius constant or frequency factor, Ea is the activation energy, R is the universal gas constant, and T is the absolute temperature.

A plot of ln k vs. 1/T gives a straight line whose slope represents the activation energy of extraction, – Ea / R, and whose intercept is the Arrhenius constant, ln A (Figure 4). Thus, the activation energy and the Arrhenius constant were calculated. These were Ea = 26.6763 kJ/mol and A = 2.0339 s^{-1}, respectively [2, 13, 15].

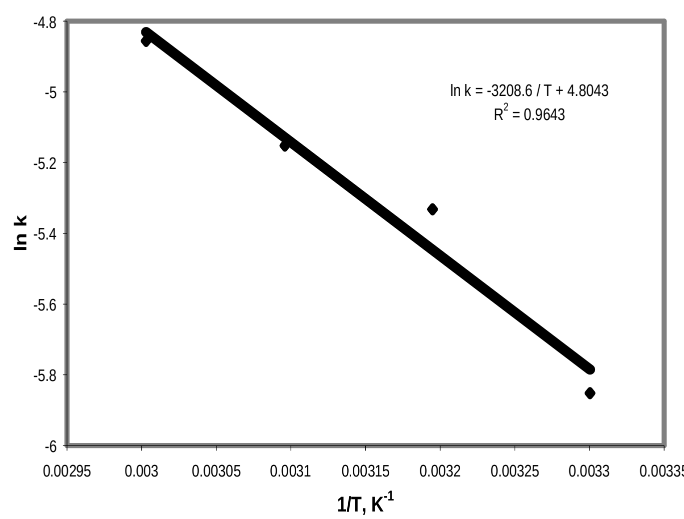

Fig. (4): A Plot of [ln k] versus [1/T] for JOC Extraction with 15 % HCl Containing n–Hexane

3.1.4 Calculation of Activation Thermodynamic Parameters:

The activation thermodynamic parameters were calculated in the following equations according to the transition state theory [2, 13, 15]:

$$A = \frac{RT}{Nh} e^{\Delta S^{\neq}/R} \quad (3)$$

$$\Delta H^{\neq} = Ea - RT \quad (4)$$

$$\Delta G^{\neq} = \Delta H^{\neq} - T\Delta S^{\neq} \quad (5)$$

where N is the Avogadro's constant, h is the Planck's constant, $\Delta S^{\neq}$ is the activation entropy, $\Delta H^{\neq}$ is the activation enthalpy, and $\Delta G^{\neq}$ is the activation free energy or Gibb's energy. These activation thermodynamic parameters are shown in table (3) for each temperature.

Table (3): The activation thermodynamic parameters for JOC extraction with15 % HCl containing n–hexane

T, K	$\Delta H^{\neq}$, kJ/mol	$\Delta S^{\neq}$, J/mol.K	$\Delta G^{\neq}$, kJ/mol
303	24.157158	-239.1416839	96.61708823
313	24.074018	-239.4116427	99.00986217
323	23.990878	-239.6731108	101.4052928
333	23.907738	-239.9266061	103.8032978

3.1.5 Calculation of Thermodynamic Parameters:

Thermodynamic parameters (ΔH, ΔS, and ΔG) for the extraction of Jatropha oil using n–hexane and 15 % HCl as solvents can be estimated using following equations [11, 13, 16]:

$$K = \frac{Y_T}{Y_u} \quad (6)$$

$$\ln K = -\frac{\Delta G}{R}\frac{1}{T} = -\frac{\Delta H}{R}\frac{1}{T} + \frac{\Delta S}{R} \quad (7)$$

where K is the equilibrium constant, Y_T is the percent oil yield at temperature T, Y_u is the percent unextracted oil, ΔH is the enthalpy change, ΔS is the entropy change, and ΔG is the free energy or Gibb's energy.

A plot of ln Y_T vs. 1/T at 60 min, gives a straight line whose slope represents the enthalpy change of extraction, – ΔH.R. Thus, the enthalpy change was calculated to be ΔH = 0.1586 kJ/mol for Jatropha seed oil extraction with 15 % HCl (Figure 5). The ΔH value obtained was indicating the physicochemical nature of the oil extraction process [11, 13, 16].

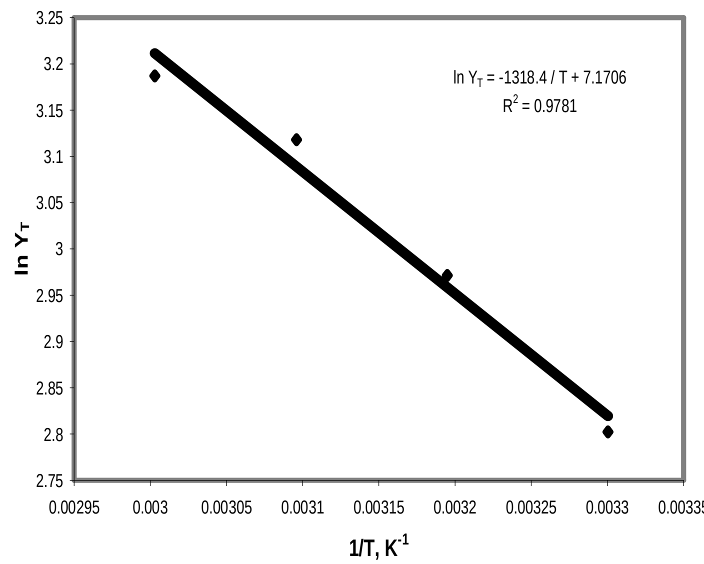

Fig. (5): A Plot of [ln Y_T] versus [1/T] for JOC Extraction with 15 % HCl Containing n–Hexane

Other thermodynamic parameters (ΔS and ΔG) and the equilibrium constant values for Jatropha seed oil extraction with 15 % HCl at 60 min, are given in table (4) for each temperature.

Table (4): The equilibrium constants (K) and the thermodynamic parameters (ΔS and ΔG) for JOC extraction with 15 % HCl containing n–hexane

T (K)	K	ΔS ($mol^{-1}.K^{-1}$)	ΔG (kJ/mol)
303	1.394449615	3.287756441	-0.837614202
313	2.222500569	7.146466889	-2.078268136
323	3.966654967	11.94700054	-3.700305173
333	5.929480901	15.27459769	-4.927865031

According to these results, the positive value of enthalpy indicates that the process is endothermic and requires energy during process. In addition, the negative value of ΔG (ΔG < 0) at 60 °C indicates that there is a decrease in the free energy, that is, the extraction process of Jatropha oil using n–hexane and 15 % HCl at 60 °C is spontaneous process, which is in agreement with previous investigations [11, 13, 16].

The reaction system initially consists of the ground Jatropha seed, aqueous acid solution and n–hexane, whereas the oil molecules are extracted from the Jatropha seeds during the extraction process, and therefore, the entropy of the mixture increases in the course of the extraction, that is the positive value of entropy change (ΔS > 0) at 60 °C indicates that the process is irreversible [11, 13, 16], while at temperatures less than 60 ºC the reaction is reversible.

3.2. Bench Scale Results:

Flow sheets representing the mass balance at optimum conditions for acid extraction (Figure 6), compared with conventional solvent extraction (Figure 7), and mechanical pressing extraction (Figure 8). Table (5) illustrates differences in the three extraction procedures.

Table (5): Comparison between different extraction procedures

Extraction Procedure	Time of Extraction, (hrs)	Temperature, (ºC)	Produced Oil, (%)
Conventional hexane	20	75	23
Aqueous acidic hexane	3	60	23.5
Mechanical pressing	0.5	60	6.595

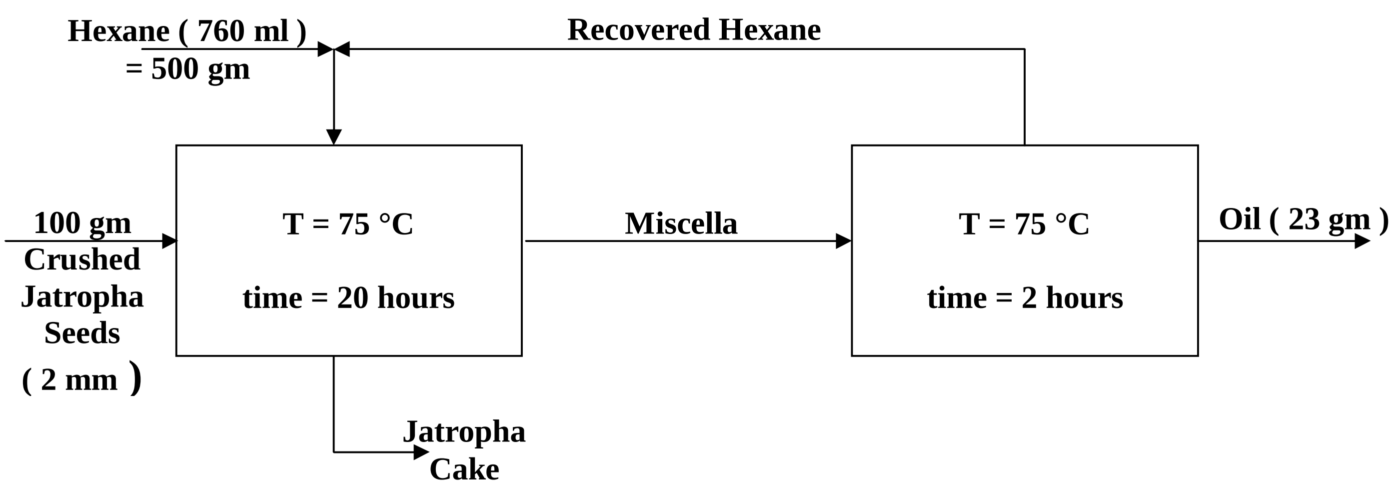

Fig. (6): Solvent Extraction of Jatropha Curcas Oil

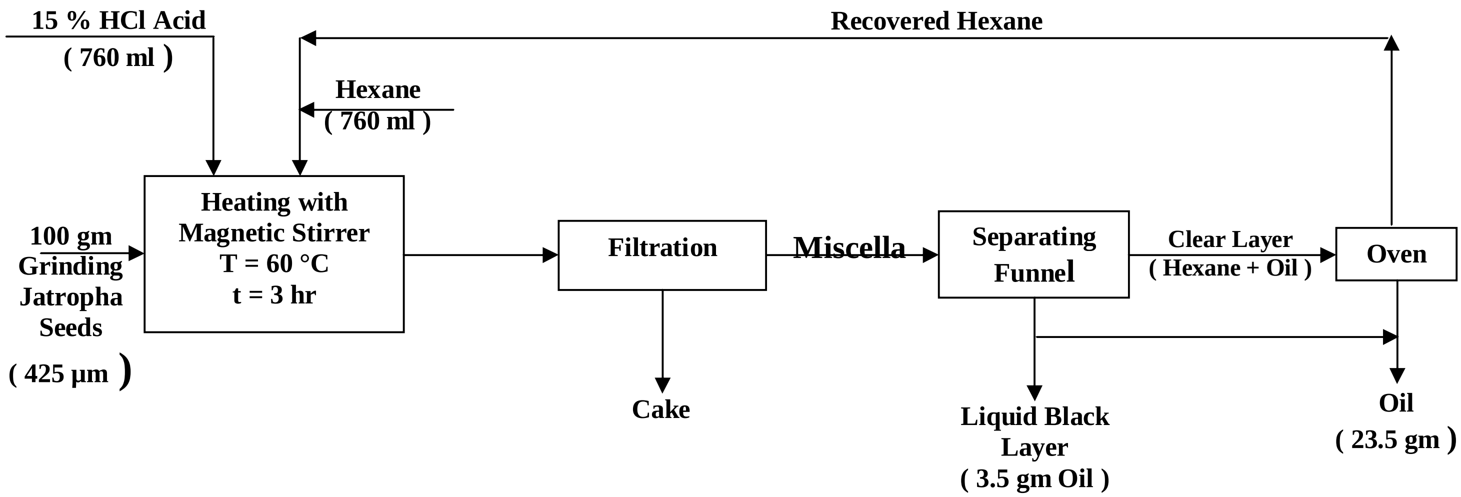

Fig. (7): Developed Oil Extraction from Jatropha Curcas Using Aqueous Acidic Hexane Solution

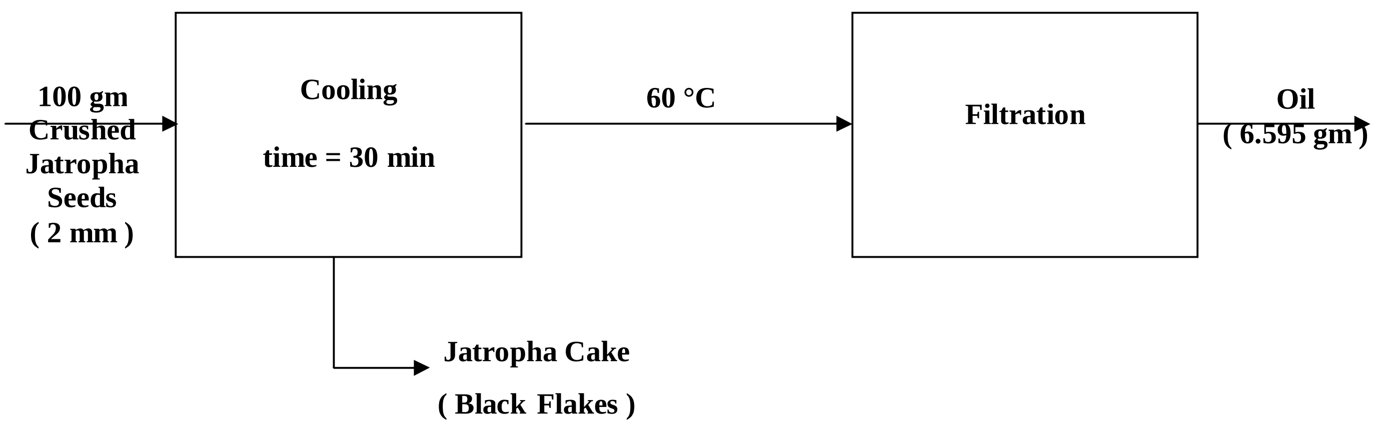

Fig. (8): Mechanical Pressing

4. Conclusion

It was found that Hydrochloric acid, HCl, was more effective and more suitable than H_2SO_4 and H_3PO_4 in the presence of n–hexane for oil extraction from Jatropha seeds. The optimum acid concentration was 15 %.

The Jatropha seed oil extraction process, using 15 % HCl containing n–hexane, has a first order kinetics.

The activation energy was Ea = 26.6763 kJ/mol, and the activation thermodynamic parameters at 60 °C were $\Delta H^{\neq}$ = 23.908 kJ/mol, $\Delta S^{\neq}$ = –239.927 J/mol.K, and $\Delta G^{\neq}$ = 103.803 kJ/mol. The enthalpy value was ΔH = 0.1586 kJ/mol, and the other thermodynamic parameters at 60 °C were calculated to be ΔS = 15.275 J/mol.K, and ΔG = –4.928 kJ/mol.

It also found that ΔH is positive, ΔS is positive, and ΔG is negative indicating that this process are endothermic, irreversible, and spontaneous.

It is concluded from table (5) that extraction time with hexane in 15 % HCl is reduced to the seventh of that with hexane pure which corresponds to less energy required and in consecutively to less cost.

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