

## Research Article

**Production of Ethyl Levulinate (an additive to biodiesel) using Paper Waste**Shalika Devi<sup>a</sup>, Himanshu Bhaskar<sup>b\*</sup>, Krishnendu Kundu<sup>b</sup> and V. R. Dahake<sup>b</sup><sup>a</sup>Department of Biotechnology and Environmental Sciences, Thapar University, Patiala (India)<sup>b</sup>Department of Biofuel, CSIR- Central Mechanical Engineering Research Institute, Centre of Excellence for Farm Machinery, Ludhiana (India)

Accepted 15 June 2013, Available online 19 June 2013, Vol.3, No.2 (June 2013)

**Abstract**

Waste papers such as old newspaper, waste paper chunks or any other paper products can be used for the production of fuel Ethyl Levulinate which can be used as an additive to the biodiesel. The utilization of the ethanol as an additive to the diesel leads to some specific problems due to the difference in their chemical properties. The Ethyl Levulinate is an ester of levulinic acid derived from the cellulose may be served as an oxygenative diesel additive. The local newspapers were used as the source of the cellulose. They were treated with the dilute sodium hydroxide (18%) at 100 °C to extract the pure cellulose and remove the lignin present in it. The paper pulp was further treated with 10 ml of hydrogen peroxide, which helps in the deinking of the newspaper. The paper pulp extracted undergoes acid catalyzed cellulose hydrolysis at 200 °C for 30 min using sulfuric acid and ethanol to produce the ester, ethyl levulinate. At the end of the reaction the extract was treated with diethyl ether which results in the formation of two layers; the upper layer is light yellow in color which is ethyl levulinate and bottom layer is dark yellow in color which is resin. The production of the levulinic acid was confirmed by spectrophotometer at 340 nm wavelength.

**Keywords:** - Paper waste; Esterification; Cellulose; Additive; Hydrolysis**Introduction**

Biodiesel is a liquid fuel that is produced by chemical processing of vegetable oil and altering its properties to make it able to perform more like petroleum diesel fuel. It was first evaluated seriously in the late 1970's but was not widely adopted at that time. The topic of biodiesel fuel has been receiving a great deal of interest recently, and both large- and small-scale manufacturers have started production at different locations throughout the world. However, many people are still uncertain about whether biodiesel is a reliable, safe fuel to use for diesel engines. A direct conversion of cellulosic wastes, including resin-bonded furniture and building waste, to levulinate esters is being investigated with the view to producing fuels, solvents, and chemical intermediates as well as other useful by-products in an inexpensive process. The acid-catalyzed reaction of cellulosic materials with ethanol or methanol at 200 °C gives good yield of levulinate and formate esters, as well as useful by-products, such as a solid residue (charcoal) and a resinous lignin residue. An initial plant design showed reasonable rates of return for production of purified ethyl levulinate and by-products. These levulinate fuels - esters using ethanol, methanol, butanol, or mixed alcohols - are certified viable additives

for gasoline and diesel transportation fuels. Levulinate fuel mixtures burn cleaner than pure hydrocarbon products.

Levulinates have many advantageous properties. They are non-toxic. Ethyl levulinate is an FDA approved food additive, and is common in perfumes and candles, and levulinic acid is used in approved skin cancer treatments. Levulinates have greater miscibility with petrochemical fuels than either soy diesel or ethanol. Thus, unlike ethanol, mixtures of levulinate and gasoline can be pipelined instead of having to be splash blended at the pump. Moreover, levulinates have lower cloud point than biodiesel, resulting in better general cold flow properties. Energy demand in India is increasing at the rate of 6% annually compared to 2% for many other countries. Currently, imported petroleum crude supplies about 70% of the energy requirement. The predicted shortage of fossil fuel encouraged the search for substitutes for petroleum derivatives. Vegetable oils, fats and their derivatives have been proposed as an alternate renewable and eco-friendly energy source. As India imports more than 40% of its edible oil requirement, it has to depend on non-edible oils for biodiesel. Various non-edible oils such as neem (*Azadirachta indica*), mahua (*Madhuca longifolia*) and jatropha (*Jatropha curcas*) are available in the country. The high energy demand in the industrialized world as well as in the domestic sector and pollution problems caused due to the widespread use of fossil fuels make it increasingly necessary to develop the renewable energy sources of limitless duration and smaller environmental

Cdr. V. R. Dahake is Chief Scientist & Scientist in Charge, Dr. Krishnendu Kundu is Sr. Scientist, Shalika Devi is MSc student and, \*Himanshu Bhaskar, corresponding author is Junior Research Fellow

impact than the traditional one. This has stimulated recent interest in alternative sources for petroleum-based fuels. An alternative fuel must be technically feasible, economically competitive, environmentally acceptable, and readily available. One possible alternative to fossil fuel is the use of oils of plant origin like vegetable oils and tree borne oil seeds. This alternative diesel fuel can be termed as "biodiesel".

Biodiesel is biodegradable and non-toxic and has low emission profiles as compared to petroleum diesel. Usage of biodiesel will allow a balance to be sought between agriculture, economic development and the environment. Chemically the oils/fats consist of triglyceride molecules of three long chain fatty acids that are ester bonded to a single glycerol molecule. These fatty acids differ by the length of carbon chains, the number, orientation and position of double bonds in these chains.

Biodiesel refers to lower alkyl esters of long chain fatty acid, which are synthesized either by transesterification with lower alcohols or by esterification of fatty acids. The possibility of using vegetable oils as fuel has been recognized since the beginning of diesel engines. Esters from vegetable oil are the best substitutes for diesel because they do not demand any modification in the diesel engine and have a high energetic yield.

### Cellulose Hydrolysis to Levulinic Acid

- Levulinic acid produced by acid hydrolysis of cellulose
- 50% yield-but production technology is not commercial
- Easily converted to ethyl or methyl ester
- Properties of Ethyl Levulinate have been examined:
  - Good lubricity, flash point
  - Blends up to 10% stable based on preliminary tests

Levulinic Acid (LA) can be produced cost effectively and in high yield from renewable feedstocks in a new industrial process. The technology is being demonstrated on a 1 ton/day scale at a facility in South Glens Falls, New York. Low cost LA can be used as a platform chemical for the production of a wide range of value-added products. This research has demonstrated that LA can be converted to methyltetrahydrofuran (MTHF), a solvent and fuel extender. MTHF is produced in >80% molar yield via a single stage catalytic hydrogenation process. A new preparation of  $\delta$ -aminolevulinic acid (DALA), a broad spectrum herbicide, from LA has also been developed. Each step in this new process proceeds in high (>80%) yield and affords DALA (as the hydrochloride salt) in >90% purity, giving a process that could be commercially viable. LA is also being investigated as a starting material for the production of di-phenolic acid (DPA), a direct replacement for bisphenol A.

### Experimental

**Materials:** Paper wastes in form of the waste newspaper were obtained locally. Chemicals used were sodium chloride, hydrogen peroxide, sulphuric acid, ethanol, diethyl ether and the various apparatus such as pressurized

reactor, hot air oven, spectrophotometer and distillation column were obtained from the Bio-fuel laboratory, CSIR-CMERI-CoEFM, Ludhiana.

### Pre-treatment / Precooking

The waste newspapers were taken 850 g and were manually crushed into small pieces. The crushed paper pieces were placed in a large vessel containing water for overnight. The experiments were performed by varying different parameters. Initially, the ratio of the cooking solution to the paper weight was altered from 1:1.5, 1:3 and 1:4.5 (paper:NaOH). The cooking solution which basically contained sodium hydroxide at 18% concentration. These three samples were then placed in hot air oven for a time of 30 min at the temperature of 30 °C. The NaOH treated paper was now crushed in the grinder forming a paper paste like solution and the excess NaOH was recycled. The waste NaOH solution contained the fibres and the lignin present in the paper. The hydrogen peroxide was added in the fixed amount to all the samples and was again heated in the hot air oven at 100 °C for 30 min. After the reaction is over paper pulp could be seen floating above the solution containing H<sub>2</sub>O<sub>2</sub>. The hydrogen peroxide helps in the deinking of paper waste.

### Hydrolysis reaction

The paper pulp was dried to remove the excess water present in it. The acid hydrolysis reaction was performed with the sulphuric acid in the presence of ethanol (25 ml) in a closed pressurized reactor at a temperature of 150 °C for 30 min. The initial amount of the paper pulp and the concentration of the sulphuric acid was varied to analyze best ratio of the chemical required for the best yield of ethyl levulinate. The concentration of the sulphuric acid was varied from 10% to 30%. After the reaction is over the paper pulp were pressed hard manually for the recovery of the ethyl levulinate. The solution so obtained was filtered off with the filter paper to remove the charcoal formed during the reaction.

The ethyl levulinate solution was neutralized by addition of the NaOH solution drop wise till the pH of the solution comes near 7.0.

### Distillation

The paper pressed solution might contain the unreacted excess ethanol solution, which was distilled off by heating it till 85 °C in the distillation column, the ethanol could be recovered for further utilization.

### Product recovery

The remaining distillate contains the resins and ethyl levulinate. Diethyl ether was added at varying amounts to the sample solution. Yellow colored solution formed at the top layer was ethyl levulinate and the dark colored bottom residue contained the resin. The resin was manually removed and ethyl levulinate was separated out.

**Results**

*Precooking*

Table 1, 2 and 3 shows the amount of the wet paper pulp obtained at different weight ratio of the paper and the NaOH solution added at the constant process parameters such as reaction time, temperature and initial concentration of the waste paper. The obtained wet paper pulp was treated with 10% H<sub>2</sub>O<sub>2</sub> in 100 ml of the water and kept in the hot air oven for 30 min. The three experiments were performed by changing the cooking solution ratio at (1:1.5, 1:3 and 1:4.5) as shown in tables 1, 2 & 3.

**Table 1:-** Weight ratio of the precooking solution 1:1.5 (paper:NaOH)

**Process parameters**

Temperature	100 °C
Time	30 min
Initial weight of NaOH solution	150 ml
Final weight of NaOH solution	70 ml
NaOH solution used up during reaction	80 ml

**After Grinding**

Paper pulp weight (wt.) 268.0 g

**Addition of H<sub>2</sub>O<sub>2</sub> (20 ml in 200 ml of water)**

Time	30 min
Temperature	100 °C
Weight of paper pulp (wt.)	255.5 g

**Table 2:-** Weight ratio of the precooking solution 1:3 (paper:NaOH)

**Process parameters**

Temperature	100 °C
Time	30 min
Initial weight of NaOH solution	300 ml
Final weight of NaOH solution	200 ml
NaOH solution used up during reaction	100 ml

**After Grinding**

Paper pulp weight (wt.) 421.5 g

**Addition of H<sub>2</sub>O<sub>2</sub> (20 ml in 200 ml of water)**

Time	30 min
Temperature	100 °C
Weight of paper pulp (wt.)	415.5 g

**Table 3:-** Weight ratio of the precooking solution 1:4.5 (paper:NaOH)

**Process parameters**

Temperature	100 °C
Time	30 min
Initial weight of NaOH solution	450 ml
Final weight of NaOH solution	375 ml
NaOH solution used up during reaction	75 ml

**After Grinding**

Paper pulp weight (wt.) 353.0 g

**Addition of H<sub>2</sub>O<sub>2</sub> (20 ml in 200 ml of water)**

Time	30 min
Temperature	100 °C
Weight of paper pulp (wt.)	348.5 g

*Esterification*

Table 4, 5 & 6 shows the recovery of product by the acid hydrolyzed esterification process carried out at different concentration of sulfuric acid and ethanol with paper pulp. Highest recovery of the product was observed at the molar ratio of precooking solution of 1:1.5 when the paper pulp was reacted with 30% sulfuric acid (25 ml) and ethanol at 150 °C for 30 min inside a pressurized reactor. After the reaction was over the ethyl levulinate was separated out by pressing the paper pulp manually and the solution was neutralized with drop wise addition of the NaOH solution. The paper solution then was distilled at 85 °C for 10 min in the distillation column. Subsequently, diethyl ether was added to separate out the resin present in the solution. The upper layer was light yellow colored ethyl levulinate and the lower ester was separated out.

**Table 4:-** Ester recovery, process parameters for weight ratio of cooking solution 1:1.5

S. No.	Material & Process Parameter	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Sample 6
01	Paper pulp (g)	40 g	40 g	40 g	20 g	20 g	20 g
02	H <sub>2</sub> SO <sub>4</sub>	10% (25 ml)	20% (25 ml)	30% (25 ml)	10% (25 ml)	20% (25 ml)	30% (25 ml)
03	Ethanol	25 ml	25 ml	25 ml	25 ml	25 ml	25 ml
04	Temperature	150 °C	150 °C	150 °C	150 °C	150 °C	150 °C
05	Time	30 min.	30 min.	30 min.	30 min.	30 min.	30 min.
06	Paper weight after reaction	12.3 g	14.2 g	17.1 g	8.6 g	10.5 g	11.4 g
07	Amount of paper weight reacted	27.7 g	25.8 g	22.9 g	11.4 g	9.5 g	8.6 g
08	Diethyl ether	35 ml	35 ml	35 ml	35 ml	35 ml	35 ml
09	Resin produced	9 g	17.3 g	21.1 g	14 g	17 g	19.4 g

**Table 5:-** Ester recovery, process parameters for weight ratio of cooking solution 1:3

S. No.	Material & Process Parameter	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Sample 6
01	Paper pulp (g)	40 g	40 g	40 g	20 g	20 g	20 g
02	H <sub>2</sub> SO <sub>4</sub>	10% (25 ml)	20% (25 ml)	30% (25 ml)	10% (25 ml)	20% (25 ml)	30% (25 ml)
03	Ethanol	25 ml	25 ml	25 ml	25 ml	25 ml	25 ml
04	Temperature	150 °C	150 °C	150 °C	150 °C	150 °C	150 °C
05	Time	30 min.	30 min.	30 min.	30 min.	30 min.	30 min.
06	Paper weight after reaction	17.2 g	17.7 g	18.1 g	8.8 g	9.2 g	9.8 g
07	Amount of paper weight reacted	22.8 g	22.3 g	21.9 g	11.2 g	10.8 g	10.2 g
08	Diethyl ether	35 ml	35 ml	35 ml	35 ml	35 ml	35 ml
09	Resin produced	9 g	11.1 g	13.3 g	7 g	7.7 g	8.2 g

**Table 6:-** Ester recovery, process parameters for weight ratio of cooking solution 1:4.5

S. No.	Material & Process Parameter	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Sample 6
01	Paper pulp (g)	40 g	40 g	40 g	20 g	20 g	20 g
02	H <sub>2</sub> SO <sub>4</sub>	10% (25 ml)	20% (25 ml)	30% (25 ml)	10% (25 ml)	20% (25 ml)	30% (25 ml)
03	Ethanol	25 ml	25 ml	25 ml	25 ml	25 ml	25 ml
04	Temperature	150 °C	150 °C	150 °C	150 °C	150 °C	150 °C
05	Time	30 min.	30 min.	30 min.	30 min.	30 min.	30 min.
06	Paper weight after reaction	20.1 g	21 g	22.2 g	10.3 g	11.5 g	12.3 g
07	Amount of paper weight reacted	19.9 g	19 g	17.8 g	9.7 g	8.5 g	7.7 g
08	Diethyl ether	35 ml	35 ml	35 ml	35 ml	35 ml	35 ml
09	Resin produced	11.3 g	19.6 g	21.1 g	8 g	9.5 g	11.0 g

#### Fuel characterization

**Cloud and Pour Point:** The cloud point of a fluid is the temperature at which dissolved solids are no longer completely soluble, precipitating as a second phase giving

the fluid a cloudy appearance. The pour point of a liquid is the lowest temperature at which it becomes semi solid and loses its flow characteristics. The cloud and pour point for ethyl levulinate are recorded in Table no. 7.

**Flash and Fire Point:** The flash point of a volatile material is the lowest temperature at which it can vaporize to form an ignitable mixture in air. The fire point of a fuel is the temperature at which it will continue to burn for at least 5 seconds after ignition by an open flame. The flash and fire point for ethyl levulinate are recorded in Table no. 7.

**Density:** The mass density or density of a material is its mass per unit volume. The symbol most often used for density is  $\rho$ . It is having higher density as compared to biodiesel as well as petro-diesel.

**Table 7:-** Characterization of fuel

Property	Ethyl Levulinate Value
<b>Molecular Formula</b>	C <sub>7</sub> H <sub>12</sub> O <sub>3</sub>
<b>Molecular Weight</b>	144.17
<b>Physical State</b>	Clear Liquid
<b>Appearance</b>	Colorless to pale yellow liquid
<b>Solubility</b>	Freely Soluble
<b>Boiling Point</b>	93-95 °C (18 mm Hg)
<b>Density</b>	1.019 g/ml at 25 °C
<b>Flash Point</b>	92 °C
<b>Fire Point</b>	89 °C
<b>Cloud Point</b>	-5
<b>Pour Point</b>	-13

## Conclusions

- A simple acid catalyzed esterification process was developed and the process parameters were standardized in order to get maximum recovery of ethyl levulinate.
- Based on the observations on the ethyl levulinate ester recovery, it was concluded that paper solution at 1:4.5 weight ratio may be reacted with ethanol at 150 °C.

reaction temperature for 30 min and then allowed to settle as biphasic layer by addition of diethyl ether to get the maximum ester recovery.

## References

- Browning B L (1990), The Chemistry of Wood. Interscience Publishers Inc., New York 242, 56-63.
- Chia M, Dumesic J A (2011). Liquid-phase catalytic transfer hydrogenation and cyclization of levulinic acid and its esters to  $\gamma$ -valerolactone over metal oxide catalysts. Chemical Communications 47, 12233-12235.
- Daniel J Hayes, J Ross, M H B Hayes, S Fitzpatrick. The Biofine Process: Production of Levulinic Acid, Furfural and Formic Acid from Lignocellulosic Feedstocks. University of Limerick, Ireland, Biofine, USA.
- Dharne S, Bokade V V (2011). Esterification of levulinic acid to n-butyl levulinate over heteropolyacid supported on acid-treated clay. Journal of Natural Gas Chemistry 20, 18-24.
- Garves K (1988). Acid catalyzed degradation of cellulose in alcohols. Journal of Wood Chemistry and Technology 8, 121-134.
- Klem D, Bertram P, Heinze T (1998). Comprehensive Cellulose Chemistry: Fundamental and Analytical Methods, John Wiley and Sons Inc., U.S.A. 1, 105-107.
- Le Van Mao R, Zhao Q, Dima G, Petraccone D (2011). New process for the acid-catalyzed conversion of cellulosic biomass (AC3B) into alkyl levulinates and other esters using a unique one-pot system of reaction and product extraction. Catalysis Letters 141, 271-276.
- Levulinic acid: a literature reference, compiled by Division of research development, A. E. Staley Mfg. Company.
- Xueyan Zheng, Richard D Gandour, Kevin J Edgar (2013). Probing the Mechanism of TBAF-Catalyzed Deacylation of Cellulose Esters. Biomacromolecules 14(5), 1388-1394.
- Rowel M R (1987). Modified Cellulosics. Academic Press Inc., New York 23-34.
- Tanghe L J, Genung L B and Mench J W (1963). In Advances in Carbohydrate Chemistry. Academic Press 193.