## ENERGY VALUATION OF HYDROXYALKANOATES AS BIOPOLYMER

## MEDIATED LIGNIN DEGRADATION OF LIGNOCELLULOSE WASTE

## <sup>1</sup>Gujar Anantkumar Jotiram, <sup>2</sup>Milind Shivaji Rohokale, <sup>3</sup>A. Dyson Bruno, <sup>4</sup>Yogesh Kumar Agarwal, <sup>5</sup>Gourav kalra

<sup>1</sup>Professor, Department of Mechanical Engineering, D. Y. Patil College of Engineering and Technology, Kolhapur-416006, India.

<sup>2</sup>Professor, Department of Mechanical Engineering, SKN Sinhgad Institute of Technology and Science, Kusgaon, (Bk) Lonavala, Pune 41040, India.

- <sup>3</sup>Assistant Professor, Department of Mechanical Engineering, PSNA College of Engineering and Technology, Kothandaraman Nagar, Tamilnadu 624622, India.
  - <sup>4</sup>Assistant Professor, Department of Civil Engineering, Jaipur Engineering College and Research Centre, Shri Ram ki nangal EPIP gate sitapura, Jaipur-302022,India.

<sup>5</sup>Assistant Professor, Department of Mechanical Engineering, Maharishi Markandeshwar (Deemed to be University) Mullana-133207, India.

#### Abstract

In this study, lignin degradation of lignocellulose waste using biopolymer as derived from agro waste. Initially, biopolymer was extracted by optimizing recovery time and rhamnolipid dose. At 50 min of recovery time and 25 % v/v of rhamnolipid dose, a higher of biopolymer (825 mg/g) was derived. The functional group of biopolymer was predicted and it is exhibited the hydroxyalkanoates group. Then, hydroxyalkanoates mediated lignin degradation of lignocellulose waste was proceeded at optimizing conditions.At 27 min of degradation time and 5 mg of hydroxyalkanoates dose, a higher lignin degradation (52 %) were descried which is higher than non treated lignocellulose waste. Further, the energy valuation of hydroxyalkanoates mediated lignin degradation per kg of lignocellulose waste was studied. During energy valuation, energy expended for centrifugation, drying, stiring, incubation, control the temperature of lignocellulose waste and hydroxyalkanoates extraction were considered as the input energy for lignin degradation steps and is measured as 217 kWh.

Energy content of lignocellulose sample after lignin degradation was considered as output and is measured as 310 kWh. Net energy was assessed by the difference of output and input energy and is espied as 93 kWh /kg of waste.

*Keywords:*Biomaterial, Hydroxyalkanoates, agro waste, ligninocellulose waste, lignin degradation

### **1.Introduction**

The developing countries GDP is mainly liable on agricultural activities for conquering a steadyfinancial growth rate in the worldwide market. Nowadays, globally industrial activities are boomed to explore the necessity of people for proper supply of food items and fuel in terms of gas or liquid, which leads to surge the agricultural products generation and also, the degradation of conservational resources. Thus, it results in the generation of tons of waste from agricultural activities and also exhaustion of natural resources [1]. Usually, agro waste also called as lignocellulose waste includes vegetable waste, fruit waste, animal waste, plant waste and other crops. In developing countries, the primary lignocellulose waste namely rice straw, wheat stalk and sugarcane bagasse are reused as propitious sources for fuels generation through ecofriendly process.But the price of these source is a primeconstraint, which may be accountable as 40-70% of net fuel generation cost [2]. The price of lignocellulose waste is usually varied which depends on seasonal harvesting at the rate of 50 to 300 USD per 1000kg whereas the biomass of municipal activities which may comprises as agro wastegaged to be 10 USD per 1000 kg [3].Food and agriculture organization reported that 40-50 % of lignocellulose waste is produced after its harvesting, processing and usage in industrial product production. The generated lignocellulose waste containing high moisture content (30-40%), which maybe made unfathomable condition during the agro waste management proceedings. The indecorous discard of lignocellulose wastedisturbs the environment byleachate formation and emanating greenhouse gases [4]. Moreover, the energy efficient fuel

generation from lignocellulose waste is constrained because occurrence of lignin biopolymer leads to ineffective hydrolysis process [5]. Thus, lignocellulose waste to be subjected to lignin degradation which is necessary to overwhelmed the hydrolysis limitation by attaining the effective bio-components extricate.

Biopolymer is called as plastic which alternate to chemically produced polymer because it is easily microbially degradable, no peril natureand easy accessibility by recovering from waste source. Biopolymer is mainly applicable for medical purpose especially surgical utensils making and food industry in terms of packing and coating of food items. Recently, commercial biopolymer plays a key role in biomass fragmentation for enhancing hydrolysis rate [6]. The above literature analysis accomplishes that no research work has been reported the impact of hydroxyalkanoates on lignocellulose waste for lignin degradation Therefore, the crucial objectives of the current study are to i) collect and characteristics of agro waste and lignocellulose waste ii) optimize recovery time and rhamnolipid dose for biomaterial extraction from agro waste iii) determination of functional group of biomaterial derived from agro waste iv)assess the lignin degradation potential of lignocellulose waste using hydroxyalkanoates v) appraise the energy input, output and net energy for hydroxyalkanoates mediated lignocellulose waste.

#### 2. Materials and Methods

#### 2.1 Biomaterial extraction from agro waste

5 kg of agro waste was collected from Gandhi market located at Trichy, Tamilnadu. The derived agro waste was crushed with mixer and kept at incubator ( $-5^{\circ}$ C) for averting further degradation. The characteristics of agro waste [7,8] was listed in Table 1. The prepared agro waste was subject to biomaterial extraction by taking 200 mL of sample in 250 mL beaker in which adding dose of rhamnolipid (1 %, 5 %, 10 %, 15 %, 20 %, 25 %, 30 % and 40 % v/v) and marked as BI1, BI2, BI3, BI4, BI5, BI6, BI7 and BI8. Then, agro waste samples were

stirred with varying recovery time (0 - 100 min) at 50 °C. The stirred agro waste was centrifuged ( $3000 \times g$  and 5 min) for separating precipitates. The ethanol solution (0.5 % v/v) was added to recovered precipitates as biomaterial and kept at room temperature. The dried biomaterial decolorized with sodium hypochlorite as adsorbent and placed in stirrer for 15 min.The decolorized biomaterial subjected to rotary evaporator for recuperating the used solvent.

Parameters	Value
pH	$7.9 \pm 0.1$
Volatile solids (VS)	$13403 \pm 157 \text{ mg/L}$
Chemical oxygen demand (COD)	$30489 \pm 108 \text{ mg/L}$
Soluble carbohydrate	$1099 \pm 18 \text{ mg/L}$
Soluble protein	$638 \pm 40 \text{ mg/L}$
Total solids (TS)	$35000 \pm 205 \text{ mg/L}$

Table 1. Characteristics of agro waste

#### 2.2 Determination of functional group of derived biomaterial using FTIR

During FTIR experiment, 5 mg of biomaterial sample was liquefied in 50  $\mu$ l of deuterated chloroform. Further, potassium bromide added to the prepared biomaterial sample and it is compressed to get salt discus. The determination of functional group of biomaterial by expose of infrared on salt discus with varying wave number (0 to 4000 cm<sup>-1</sup>) [9].

#### 2.3 Impact of hydroxyalkanoates on lignocellulose waste for lignin degradation

Bagasse waste of sugar production factory was derived from sugar mill located at Aduthurai, Tamil Nadu. The derived bagasse was dried at oven (50- 70  $^{\circ}$ C) and then, grinded well to obtain a semi-coarse powder form of bagasse waste. Then, the prepared bagasse waste was diluted with normal water in the ratio of (sample (1): water (3)) and kept in incubator ( -5  $^{\circ}$ C)

for further use in lignin degradation study. The characteristics of bagasse waste as follows pH-8.2  $\pm$  0.2, cellulose (% TS)- 30, lignin (% TS)- 24 and TS- 35871  $\pm$  102 mg/L. For lignin degradation, 100 mL of diluted bagasse waste was taken in beaker in which adding different dose of derived hydroxyalkanoates (0.5, 1, 3, 5, 7, 9, 10 mg) with degradation time (0 to 40min) at 70 °C. The lignin degradation was assessed by acetyl bromide method suggested by Sethupathy and Sivashanmugam [10]. Energy valuation of hydroxyalkanoates mediated lignin degradation of lignocellulose waste was proceeded based on the valuation steps desribed by Sethupathy etal .[11].

#### 3. Results and Discussion

#### 3.1 Extraction of biomaterial from agro waste

Figure 1 signifies the impact of recovery time and rhamnolipids dose on biomaterial extraction from agro waste. From Figure 1, it is espied that biomaterial extraction surgeprogressively from 0 to 100 min and rhamnolipid dose (1% to 40 % v/v). At 50 min of recovery time, a higher biomaterial was found to be 825 mg/g with a dosage of 25 % v/v of rhamnolipid. Then, biomaterial yield was diminished from 60 to 100 minwith respect to rhamnolipid dose. The reason for diminution in biomaterial yield is extended exposure of rhamnolipid dose on agro waste resulting in biomaterialdegradation [12]. The recovered biomaterial was decolorized with sodium hypochlorite to acquire decolorized biomaterial with 10 % loss. Therefore, these deliberations decided that 50 min of recovery time and 25 % v/v of rhamnolipid dose were optimized experimental factors for biomaterial extraction from agro waste.



Figure 1. Impact of recovery time and rhamnolipid dose on agro waste for biomaterial extraction

## **3.2 FTIR analysis**

The functional group of extracted biomaterial from agro waste was assessed using FTIR and it is depicted in Figure 2.From Figure 2, it is found that the peak (X1) at 2919 cm<sup>-1</sup>signifies methylene group, the peak (X2) at 1722 cm<sup>-1</sup>shows C=O distending group, the peak (X3) at 1452 cm<sup>-1</sup>infersunification of C-H bond in CH<sub>2</sub> compund, the peak (X4) at 1365 cm<sup>-1</sup> denotes CH<sub>3</sub> group, the peak (X5) at 1270 cm<sup>-1</sup> exemplifies C-O distending group and the peak at 1041 cm<sup>-1</sup> (X6) specifies C-O bond of ester component. From these peaks reflects the fuctional group of hydroxyalkanoatesas biomaterial which extracted from agro waste.



Figure 2. Determination of function group of extracted biomaterial from agro waste

## 3.3 Hydroxyalkanoates mediated lignin degradation and lysification of lignocellulose waste

Figure 3 depicts the hydroxyalkanoates mediated lignin degradation and lysification of lignocellulose waste.Lignin degradation of lignocellulose waste was examined, because lignin molecule acts asprimary barrier in fermentation process resulting in amplified biomass degradation time, deficiency in dilapidation of bio-components and low energy generation [13]. From Figure 3, the lignin degradation was hiked with degradation time (0 to 27 min) and hydroxyalkanoates dose (0.5 to 7 mg). At 27 min of degradation time and 5 mg of hydroxyalkanoates dose, a higher lignin degradation (52 %) were descried. Further augmenting degradation time (> 27 min), no specific progress in lignin degradation for all hydroxyalkanoates dose. Also, lysisfication is investigated and is shown in Figure 3b. From Figure 3b, 5 mg of hydroxyalkanoates dose exhibited higher lysification (25.5 %) compared to non treated lignocellulose waste (0.5 %).Therefore, these deliberations decided that 27min

of degradation time and 5 mg of hydroxyalkanoates dose were optimized experimental factors for lignin degradation and lysification of agro waste.



**Figure 3.** Hydroxyalkanoates mediated lignocellulose waste treatment a) lignin degradation b) lysification

# 3.4 Energy valuation of hydroxyalkanoates mediated lignin degradation of lignocellulose waste

Table 2 shows the energy valuation of hydroxyalkanoates mediated lignin degradation of lignocellulose waste. During energy valuation, energy expended for centrifugation, drying,

stiring, incubation, control the temperature of lignocellulose waste and hydroxyalkanoates extraction were consider as the input energy for lignin degradation steps and is measured as 217 kWh. Energy content of lignocellulose sample after lignin degradation was considered as output and was measured as 310 kWh. Net energy was assessed by the difference of output and input energy and is espied as 93 kWh /kg of waste. The above energy valuation steps indicates that hydroxyalkanoates mediated lignin degradation of lignocellulose waste was espied as energy effective method.

 Table 2. Energy valuation of hydroxyalkanoates mediated lignin degradation of

 lignocellulose waste

S.no	Factors	Hydroxyalkanoates	Unit	
	Energy valuation per kg of lignocellulose waste			
1	Average surge in lignin degradation	31	m <sup>3</sup>	
2	Energy content of lignocellulose sample after lignin degradation	310	kWh	
3	Energy expended for centrifugation	32	kWh	
4	Energy expended for stirring	55	kWh	
5	Energy expended for incubation	28	kWh	
6	Energy expended for drying	70	kWh	
7	Energy spent to control the temperature of sample	10	kWh	
8	Energy spent for hydroxyalkanoates extraction	22	kWh	
9	Total energy applied (S.no. +(3 to 8))	217	kWh	
10	Net energy (2-9)	93	kWh	

#### 4. Conclusion

Lignin degradation potential of hydroxyalkanoates was investigated through a ecofriendly process.Initially, hydroxyalkanoates was extracted by optimizing recovery time (50 min) and rhamnolipid dose (25 % v/v).The functional group of biopolymer was predicted as hydroxyalkanoates group.Then, hydroxyalkanoates mediated lignin degradation of lignocellulose waste was proceeded in which 52 % of lignin degradation descried at optimun conditions.Moreover, energy valuation was done in which hydroxyalkanoates mediated lignin degradation got net energy of 93 kWh /kg of lignocellulose waste. Therefore, the propsed study results implies that the hydroxyalkanoates mediated lignin degradation as energy effective method.

#### References

- Cesaro, A., Belgiorno, V.,2013. Sonolysis and ozonation as pretreatment for anaerobic digestion of solid organic waste. Ultrason Sonochem 20, 931-936.
- Bussemaker, M.J., Zhang, D.,2013. Effect of ultrasound on lignocellulosic biomass as pretreatment for biorefinery and biofuel applications. Ind. Eng. Chem. Res.52,3563-3580.
- Shanthi, M., Rajesh Banu, J., Sivashanmugam, P., 2018. Effect of surfactant assisted sonic pretreatment on liquefaction of fruits and vegetable residue: Characterization, acidogenesis, biomethane yield and energy ratio. Bioresour Technol 264, 35–41.
- 4. Mahato, R.K., Kumar, D., Rajagopalan, G., 2020. Biohydrogen production from fruit waste by Clostridium strain BOH3. Renewable Energy 153,1368–1377.
- 5. Nagula,K.N., Pandit, A.B., 2016. Process intensification of delignification and enzymatic hydrolysis of delignified cellulosic biomass using various process intensification techniques including cavitation. Bioresours. Technol. 213, 162-168.

- 6. Du, G., Yu, J.,2002. Green technology for conversion of food scraps to biodegradable thermoplastic polyhydroxyalkanoates. Environ Sci Technol 36, 5511–6.
- Sethupathy, A., Arun, C., Ravi Teja, G., Sivashanmugam, P., 2019. Enhancing hydrogen production through anaerobic co-digestion of fruit waste with biosolids. J Environ Sci Heal - Part A Toxic/Hazardous Subst Environ Eng 54, 553–9.
- Sethupathy, A., Ravi Teja, G., Arun, C., Sivashanmugam, P., 2018. Study on optimization of co-digestion process parameters for enhancing biohydrogen production using response surface methodology. Energy Sources, Part A Recover. Util. Environ. Eff. 40, 1753–1764.
- Sethupathy, A., Sivashanmugam, P., 2019. Investigation on ultrasonication mediated biosurfactant disintegration method in sludge flocs for enhancing hydrolytic enzymes activity and polyhydroxyalkanoates. Environ Technol 40, 3547-60.
- 10. Sethupathy, A., Sivashanmugam, P., 2021. Amelioration of methane production efficiency of paper industry waste sludge through hydrolytic enzymes assisted with poly3hydroxybutyrate. Energy 214, 119083.
- Sethupathy, A., Sivashanmugam, P., 2018. Enhancing biomethane potential of pulp and paper sludge through disperser mediated polyhydroxyalkanoates. Energy Convers Manag. 173, 179–86.
- Takabatake, H., Satoh, H., Mino, T., Matsuo, T.,2002. PHA (polyhydroxyalkanoate) production potential of activated sludge treating wastewater. Water Sci Technol 45, 119–26.
- Gayathri, T., Kavitha, S., Adish Kumar, S., Kaliappan, S., Yeom, I.T., Rajesh Banu.
   J.,2015. Effect of citric acid induced deflocculation on the ultrasonic pretreatment efficiency of dairy waste activated sludge. Ultrason Sonochem 22, 333–40.