

**OPTIMIZATION OF COMBINED WASHING AND
TORREFACTION PRETREATMENT FOR IMPROVING
FUEL PROPERTIES OF RICE STRAW: AN
EXPERIMENTAL STUDY**

C.L.W. Dissanayake

218099J

Master of Philosophy

Department of Chemical and Process Engineering

University of Moratuwa

Sri Lanka

August 2024

**OPTIMIZATION OF COMBINED WASHING AND
TORREFACTION PRETREATMENT FOR IMPROVING
FUEL PROPERTIES OF RICE STRAW: AN
EXPERIMENTAL STUDY**

C.L.W. Dissanayake

218099J

Thesis submitted in partial fulfilment of the requirements for the degree

Master of Philosophy

Department of Chemical and Process Engineering

Faculty of Engineering

University of Moratuwa

Sri Lanka

August 2024

DECLARATION

I declare that this is my own research, and this thesis does not incorporate without acknowledgment any material previously published or submitted for a Degree or Diploma in any other university or institute of higher learning, and to the best of my knowledge and belief, it does not contain any material previously published or written by another person except where the acknowledgment is made in the text. I retain the right to use this content in whole or part in future works (such as articles or books).

Signature:

Date: 12.08.2024

C.L.W.Dissanayake

The above candidate has carried out research for the MPhil thesis under my supervision. I confirm that the declaration made above by the student is true and correct.

Signature of the supervisor:

Date: 12/08/2024

Dr. R.M.D.S. Gunarathne

Signature of the supervisor:

Date: 12/08/2024

Dr. S. A. D. T. Subasinghe

DEDICATION

To my parents, for their endless love, support, and encouragement throughout this journey.

ACKNOWLEDGEMENT

I would like to express my sincere gratitude to my supervisors, Dr. (Mrs) Duleeka Sandamali Gunarathne and Dr. Dilantha Thushara Subasinghe for guiding and mentoring me through this research. I am very grateful for all the advice, comments, and valuable time dedicated to the improvement of the output of this research study.

Also, I would like to sincerely acknowledge Senior Prof. Padma Amarasinghe, and Prof. Manisha Gunasekera for their valuable support, feedback, and advice throughout the progress evaluation of this research. I am also sincerely grateful to Prof. Wei-Hsin Chen for his guidance in this research.

I would like to express my sincere gratitude to my colleague Udy Devaraja for her support and guidance in this research.

Further, I would like to thank all the academic and non-academic staff at the Department of Chemical and Process Engineering, Department of Material Science and Engineering, and Department of Mechanical Engineering for providing support by facilitating the laboratory and assistance.

Finally, I would like to acknowledge the Senate Research Committee Grant with long-term grant No. SRC/LT/2020/03 at the University of Moratuwa, Sri Lanka for providing financial assistance for this research.

ABSTRACT

Washing and torrefaction pretreatment of biomass is effective in addressing limitations such as low energy density, high moisture content, and high ash content for energy applications. Combining both methods for the combustion or cofiring feedstock such as rice straw is beneficial for the energy industry. The present study was conducted in lab-scale by varying the process parameters to analyze and optimize the combined pretreatment process to improve the fuel properties of rice straw. Thermogravimetric analysis results of rice straw showed a significant thermal stabilization for water- and acid-washed samples compared to raw rice straw. After analyzing the lab scale washing experiments, an optimum temperature of 47 °C, 30 mins washing time, and, 23:1 liquid-to-solid ratio were obtained giving 25.24 % of ash removal for water-washing. For the acid-washing, optimized results were a washing time of 30 mins and a liquid-to-solid ratio of 40:1 giving an ash removal of 30.53 %. Calculated slagging, fouling, and bed agglomeration indices suggested that washed rice straw had a lower tendency for slagging, fouling, and agglomeration compared to the untreated sample while acid washing gave the most promising results. The torrefaction experiment results indicated that the mass loss was increased with the temperature giving the highest mass loss (47.57 %) at 300 °C. Carbon content and higher heating values were increased with the torrefaction temperature while oxygen content and energy yield were decreased. Optimum conditions obtained from the combined washing and torrefaction are 30 minutes residence time, 246 °C, and 256 °C torrefaction temperature for acid-washed and water-washed rice straw samples respectively. FTIR analysis showed the structural changes and reduction in intensity in chemical bonds after the pretreatment implied good fuel properties of rice straw. The combustion study indicated that an optimized acid-washed torrefied rice straw sample had the highest combustion performance compared to both raw rice straw and coal. Hence, the combined washing and torrefaction process improved the fuel quality of rice straw by reducing ash-related problems and improving combustion properties.

Keywords: Biomass, Rice Straw, Water Washing, Acid Washing, Torrefaction, Optimization, Combustion

TABLE OF CONTENTS

1	Introduction	1
2	Literature Review	4
2.1	Biomass as an energy source.....	4
2.2	Characterization of biomass	5
2.3	Challenges of biomass as an energy source	8
2.4	Overview of washing technology	10
2.4.1	Washing parameters	10
2.4.2	Properties of washed biomass	14
2.4.3	Combustion properties of washed biomass.....	16
2.4.4	Washing Kinetics	17
2.5	Overview of Torrefaction.....	19
2.5.1	Introduction to torrefaction	19
2.5.1	Torrefaction parameters	20
2.5.2	Biomass properties after the torrefaction process	22
2.5.3	Combustion properties of torrefied biomass	23
2.5.4	Torrefaction kinetics	24
2.6	Combined pretreatment methods	25
2.6.1	Pre-washing of biomass with torrefaction.....	26
2.6.2	Post-washing of biomass with torrefaction.....	27
2.7	Optimization of process parameters.....	28
3	Research Methodology.....	30
3.1	Sample selection and preparation	30

3.2	Analyze the leaching behavior of rice straw in the water and dilute acid.....	31
3.3	Analyze the torrefaction behavior of water-washed and dilute acid-washed rice straw. 36	
3.4	Optimizing the process parameters	38
3.4.1	Washing parameter optimization	39
3.4.2	Torrefaction optimization.....	40
3.5	Study the combustion behavior of rice straw pretreated with combined washing and torrefaction.	41
4	Results and Discussion.....	44
4.1	Thermal behavior of rice straw	44
4.1.1	Raw rice straw sample	44
4.1.2	Pretreated rice straw samples	45
4.2	Kinetic study for water washing pretreatment	46
4.2.1	Effect of the L/S ratio on the water washing of rice straw.....	46
4.2.2	Effect of washing temperature on the leaching behavior.....	52
4.3	Kinetic study for acid washing pretreatment	55
4.3.1	Effect of the L/S ratio on the acid washing of rice straw.....	55
4.4	Analysis of sample properties	57
4.5	Pretreatment performance for water washing and acid washing.	59
4.5.1	Water washing pretreatment.	59
4.5.2	Construction of mathematical model for water washing experiment	60
4.5.3	Variation of ash content reduction % with two simultaneous variables ..	63
4.5.4	Effect of single factors on ash removal.....	65

4.5.5	Prediction of optimal results	66
4.5.6	Acid washing pretreatment	67
4.5.7	Construction of mathematical model for acid washing experiment	68
4.5.8	Variation of ash content reduction % with two simultaneous variables ..	70
4.5.9	Effect of single factors on ash removal.....	71
4.5.10	Prediction of optimal results	72
4.6	Ash composition analysis.....	73
4.6.1	Mineral composition	73
4.6.2	Slagging and fouling indices.....	76
4.7	Ash melting behavior of raw and washed rice straw	78
4.8	Analysis of sample properties for torrefied rice straw samples	83
4.8.1	Color of the torrefied and raw rice straw	83
4.8.2	Proximate analysis of torrefied rice straw.....	85
4.8.3	Ultimate analysis of torrefied rice straw	86
	Effect of temperature and time on solid yield, HHV, energy yield, and EMCI	
	87	
4.8.4	87
4.8.5	Solid yield variation of torrefied rice straw	90
4.8.6	Higher heating value (HHV) variation of torrefied rice straw	92
4.8.7	Energy yield variation of torrefied rice straw	93
4.8.8	Energy mass co-benefit index (EMCI) variation of torrefied rice straw .	94
4.8.9	Prediction of optimal results	95
4.8.10	Mass and Energy flow analysis.....	96

4.9	Fourier Transform Infrared (FTIR) Analysis	99
4.10	The combustion behavior of raw and pretreated rice straw	101
4.10.1	Analysis of combustion characteristics	101
	Economic aspects of the combined pretreatment process.....	107
4.11	107
5	Conclusion	110
6	References	113

LIST OF FIGURES

Figure 3.1-Rice straw samples	30
Figure 3.2-Torrefaction reactor	37
Figure 3.3-Schematic diagram of the torrefaction reactor setup.....	37
Figure 3.4-TGA/DTG curves for rice straw.....	42
Figure 4.1-Thermal behavior of raw rice straw	44
Figure 4.2-(a) TGA curves with a heating rate of 10 °C /min, (b) DTG curves with a heating rate of 10 °C /min.....	45
Figure 4.3-Variation of EC with washing time at dissimilar L/S ratios at 35°C	46
Figure 4.4-Variation of EC with washing time at dissimilar L/S ratios at 50°C	47
Figure 4.5-Variation of EC with washing time at dissimilar L/S ratios at 70°C	47
Figure 4.6-Second order kinetic model variations for different L/S ratios at (a)35°C (b)50°C and (c)70°C	49
Figure 4.7-Variation of EC with washing time at different temperatures at 20 L/S ratio	52
Figure 4.8- Variation of EC with washing time at different temperatures at 50 L/S ratio	52
Figure 4.9- Variation of EC with washing time at different temperatures at 80 L/S ratio	53
Figure 4.10- Second-order kinetic model variations for different temperatures at (a) 20:1 (b) 50:1 and (c) 80:1.....	54
Figure 4.11-Variation of EC with washing time at different L/S ratios.....	55
Figure 4.12-Second order kinetic model variations for different L/S ratios at 35°C	56
Figure 4.13-Proximate analysis of water-washed rice straw at different test parameters	58
Figure 4.14-Proximate analysis of acid-washed rice straw at different test parameters..	58

Figure 4.15-Relationship between experimental and predicted values of ash removal percentage	63
Figure 4.16- Contour plot for ash content reduction % for each parameter variation of water-washed rice straw.....	64
Figure 4.17-Variation of ash content reduction with individual factors	65
Figure 4.18-Contour plot of optimum ash content reduction percentage	67
Figure 4.19-Relationship between actual and predicted values of ash content reduction percentage for acid washing.....	70
Figure 4.20-Contour plot for ash content reduction %	71
Figure 4.21-Variation of ash removal with individual factors	72
Figure 4.22-Contour plot of optimum ash removal percentage	73
Figure 4.23-Behaviour of ash composition with the removal percentage(wt.%).	76
Figure 4.24-SEM images for raw and optimum washed ash samples at different temperatures showing ash melting behavior	80
Figure 4.25-Color variation of raw and torrefied rice straw (water washed) samples.	83
Figure 4.26-Color variation of raw and torrefied rice straw (acid washed) samples.....	83
Figure 4.27-Proximate analysis of raw and torrefied rice straw	85
Figure 4.28-Ultimate analysis of raw and torrefied rice straw.....	86
Figure 4.29-Van Krevelen diagram for raw and torrefied rice straw.....	86
Figure 4.30-Solid yield variation of torrefied samples	91
Figure 4.31-HHV variation of torrefied rice straw	92
Figure 4.32-Energy yield variation of torrefied rice straw	93
Figure 4.33-Contour plot for EMCI of torrefied rice straw.	95

Figure 4.34-Sankey diagrams of (a) Solid yield for water-washed torrefied RS (b) Solid yield for acid-washed torrefied RS	97
Figure 4.35- Sankey diagrams of (a) Energy yield for water-washed torrefied RS (b) Energy yield for acid-washed torrefied RS.....	98
Figure 4.36-FTIR Spectrum of raw and upgraded rice straw by washing and torrefaction	99
Figure 4.37-TGA/DTG curves of raw (Raw RS)/water washed (Water W RS)/acid washed (Acid W RS)/acid washed torrefied (Acid W T RS) and water washed torrefied (Water W T RS) rice straw showing the combustion behavior.	101
Figure 4.38- General process of combined washing and torrefaction of rice straw	107

LIST OF TABLES

Table 2.1-Biomass Categorization	4
Table 2.2-Characterization of biomass compared to coal	6
Table 2.3-Torrefaction Process Stages	20
Table 3.1-Washing parameters	33
Table 3.2-Analytical measurement	33
Table 3.3-Standard test methods for proximate and HHV analysis	34
Table 3.4- Torrefaction parameters	36
Table 3.5-Experimental procedure for water washing.	39
Table 3.6-Experimental procedure for acid washing	40
Table 3.7- Torrefaction experimental procedure	40
Table 4.1-Experimental and calculated values of kinetic study for water washing.	49
Table 4.2-Calculated kinetic parameters for different L/S ratios.	51
Table 4.3-Experimental and calculated values of kinetic study for acid washing.	56
Table 4.4-Calculated kinetic parameters for different L/S ratios at 35°C	57
Table 4.5-Solid yield, Moisture content, Ash content, and Ash content reduction % at different test parameters after water washing.	59
Table 4.6-ANOVA for ash removal percentage before removal of insignificant terms	60
Table 4.7-Statistic analysis of the fitness of data with ANOVA for ash removal percentage	61
Table 4.8-Fit Statistics for the developed model	62
Table 4.9-Optimized conditions for water washing experiment	67
Table 4.10-Solid yield, Moisture content, Ash content, and Ash removal % at different test parameters after acid washing	68

Table 4.11-Statistic analysis of the fitness of data with ANOVA for ash content reduction percentage	69
Table 4.12-Optimized conditions for acid washing experiment	72
Table 4.13-Slagging and fouling index values for ash samples	77
Table 4.14-EDS data for SEM analysis of rice straw ash at different temperatures	82
Table 4.15-Solid Yield, HHV, Energy Yield, and EMCI of torrefied rice straw	87
Table 4.16-ANOVA of response surface model for each response	88
Table 4.17-Optimized conditions for combined cashing and torrefaction experiment	96
Table 4.18-Combustion parameters of raw and pretreated rice straw	103

LIST OF ABBREVIATIONS

Abbreviation	Description
AC	Ash Content
APBO	Aqueous Phase Bio-Oil
BBD	Box-Behnken Design
CCD	Central Composite Design
CV	Calorific Value
C.V.	Coefficient of Variation
DTG	Differential Thermogravimetry
EC	Electrical Conductivity
EDS	Energy Dispersive Spectroscopy
FC	Fixed Carbon
HHV	Higher Heating Value
L/S	Liquid-to-Solid
MC	Moisture content
RSM	Response Surface Methodology
SEM	Scanning Electron Microscopy
TGA	Thermo-Gravimetric Analysis
VM	Volatile Matter