# Evaluation of Co-torrefaction Performance of Coffee Bean Ground and Risk Husk Mixture for Bio-Solid Production



By Abdul Waheed

# School of Chemical and Materials Engineering National University of Sciences and Technology 2022

# **Evaluation of Co-torrefaction Performance of Coffee Bean Ground and Risk Husk Mixture for Bio-Solid**

# **Production**



Name: Abdul Waheed Reg. No: 00000318010

# This thesis is submitted as a partial fulfillment of the requirements for the degree of

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Supervisor Name: Dr. Salman Raza Naqvi

School of Chemical and Materials Engineering (SCME) National University of Sciences and Technology (NUST) H-12 Islamabad, Pakistan October, 2022

# Dedication

By the grace of Almighty Allah, who is the most Beneficent and the most merciful.

This research is dedicated to my parents, who have always been my source of guidance and support.

To my supervisor who shared her knowledge, gave advice and encouraged me to fulfillmy tasks.

And to all my fellows, with whom I worked with and shared good memories.

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### Abstract

Co-torrefaction is a thermal process is used to torrefied blending biomass at 200-300°C in an inert atmosphere to enhance its fuel properties such as increasing of heating value and carbon content and decreasing the volatile matter or oxygen content. Co-torrefaction of several biomass may be a viable solution since it not only produces biofuels but also addresses waste treatment concerns blending two or more bio waste streams independently at variable blending ratios enhances the quality of the biofuel and alleviates waste management concerns. When biomass waste is blended with other waste materials to create a better-quality solid fuel product, a synergistic effect on mass and energy yields, as well as product qualities, was seen. Co-torrefied biomass as an elemental composition equivalent to that of anthracite and bituminous coal. Different reactor types, such as fixed bed, fluidized bed, and conventional bed reactors, are used for co-torrefaction, in which different biomass blends with optimized blend ratios are combined and the torrefaction process occurs to not only increase the biochar yield and heating value, but also the capacity to adsorb carbon dioxide. Because of this, the procedure must be a viable, green, and sustainable one that does not generate any pollution. This study discusses the impact of temperature on torrefaction of rice husk (RH), coffee bean ground, and their different blending ratios. The blending ratio used in this experiment is CBG: RH (50:50) RH: CBG (75:25), RH: CBG (25:75) ratios in %, RH100%, and CBG 100%. The array of experiments for co-torrefaction is performed using a lab scale tube furnace. The fiber structure is ruptured by varying the torrefaction temperature from (200,225,250,275 and 300°C). The increase of temperature resulted in the decreases of mass yield, energy yield, and oxygen to carbon atomic ratio. In addition, the torrefaction index on a yield basis (weight loss, severity index, and torrefaction index) is enhanced at elevated temperature. The high carbon content and better fuel properties were found for CBG 100% and blending ratio of (CBG: RH (75:25)) rice husk and coffee bean ground at 300°C for 60min. The resulted data of this investigation indicate that torrefaction is an effective pretreatment process to improving rice husk and coffee bean ground fuel properties.

Keywords: Biomass; Rice husk; Coffee bean ground; Co-Torrefaction; Blending ratio

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# Acronyms

High Heating Value:	HHV
Mass Yield:	MY
Energy Yield:	EY
Wet Torrefaction	WT
Calorific Value	Cv
Optoelpctronic sludge	OS
Passiflora edulis shells	PEsh
Empty Fruit Branches:	EFB
Pistacho husk:	PH
Torrefaction severity index	TSI
Weight loss	WL
Index of co-torrefaction	I <sub>torr</sub>
Mangifera indica seed	Mlse
Energy-mass co-benefit index	EMCI
Fourier transform infrared spectrometer	FTIR

# **Chapter 1**

## Introduction

#### 1.1 Background

The fossil fuels are extensively used from last two centuries to meet the energy demand of growing population and development of globe. The increased greenhouse gas emission due to rampant use of fossil fuels has raised environmental and sustainability concerns. This has also consequences in global energy crisis. To address growing energy demands, an alternative energy source is long overdue. Septic sludge and woody biomass fuels, which now account for 10% of world energy production, are regarded a better alternative than fossil fuels in terms of renewable energy sources[1]. Because 56 percent of renewable energy comes from biomass, 26 percent from solar energy, 11 percent from wind power, and 5 percent from geothermal energy, Manzano et al. claimed that biomass has been the focus of renewable energy research for the last 30 years[2]. The percentage of energy generated from renewable sources and biofuels will rise from 2 to 27% in the future[3]. Because lignocellulosic biomass is abundant in supply and has a lesser ecological impact, research and development into its use is a major focus.

Dry biomass output in the globe is estimated at 220 billion metric tons a year, making lignocellulosic biomass the world's greatest sustainable energy source. Because it accounts for 14% of global energy consumption, lignocellulosic biomass is often referred to as the "single source of energy." [4]. **Fig 1** shows an increase in global biomass output from 2012 to 2016 of 19 million tons to 25 million tons, as reported by the UN food and agricultural agency.



Figure 1:World biomass production during 2012-2014 [5].

A previous study found that torrefaction can enhance the properties of biomass to a certain extent [1], such as reducing the raw biomass's moisture content, resulting in a rise in energy density and heating value[2]. Additionally, because raw biomass's hygroscopic characteristic has been inherently transformed to hydrophobic, co-torrefied fuel enjoys the advantages of a hydrophobic fuel properties[3].



Figure 2: Number of publications in Co- torrefaction process VS year retrieved from Scopus database (02-10-2022).

#### 1.2 Feedstock's

#### **1.2.1 Lignocellulosic Biomass**

Lignocellulosic biomass refers to any organic substance that may be burnt and utilised as a fuel. In order to produce a variety of liquid fuels, bio-oils, and bio-solids, lignocellulosic biomass is the most practical energy resource. Lignocellulosic biomass includes woody and non-woody materials including cotton stalks and rice husk as well as food waste such as sugarcane bagasse and grass and plant leaves (see **Fig 3**).

There are three distinct types of biomass: primary, secondary, and tertiary lignocellulosic. Primary biomass, such as woody plants, oil seeds, rice husks, maize cobs, rice straw, and tree bark, may be produced directly from the soil using solar energy. Chemical, physical, and biological processing of secondary biomass resources may provide secondary biomass as a byproduct. Animal fats, used vegetable oil, packaging wastes, and building debris all fall under the category of tertiary biomass. Cellulose, hemicellulose, lignin, and extractives are the main constituents of each. Bio-solids, Bio-oils, gases, and chemicals made from lignocellulosic biomass.



Figure 3: Types of woody and non-woody biomass.

#### 1.2.2 Rice husk

Rice husk is a potential feedstock for energy production that is available in abundant quantity at various parts of world. Rice husk is very important biomass composed of hemicellulose, cellulose,

and lignin, in which the percentage of cellulose and hemicellulose is more than lignin. Raw rice husk has a low calorific value, high oxygen content, high moisture content, and large particle size [4].

Milled Rice Production for Year 2019/2020 (Million Metric



The Production of rice husk in different countries is shown in Fig 4.

Figure 4: Production of rice husk in different countries [5].

#### 1.2.3 Coffee bean ground

A remarkable 10 billion kilograms of coffee beans are used each year, making it one of the most widely traded commodities in the world. During the manufacture and brewing of instant coffee, a large amount of solid residues known as coffee waste (Spent coffee grounds) is formed. Lignin, protein, and carbs make coffee bean grinds an ideal feedstock for the production of bioethanol and biodiesel, as well as solid fuel [6]. Coffee bean ground is an agricultural waste containing high moisture content which reduced its value to use as an energy source because of high cost of moisture removal [7]. Various methods are adopted to convert this low-fuel feedstock into high-value fuel [8].

The import of coffee bean ground in different state is as follow:



Year

Figure 5: Production of coffee bean in different countries [9].

#### **1.3 Co-torrefaction**

Co-torrefaction is the process in which two biomass blends go for a torrefaction process and convert in to bio solid. The **Fig 6** illustrates the process of co-torrefaction. In this figure two residual/waste biomass blend together at various ratio 0:100,25:75,50:50. This blending biomass enter in to tube furnace for torrefaction. This tube furnace provide nitrogen as a inert media so that process occur in the absence of oxygen. The sample is taken in crucible and enter in to a mid of furnace where heating rate is 10 °C/min and Temperature range is 200-300 °C at residence time. Three products (bio-oil, bio-solid, bio-gas) is obtain from tube furnace after torrefaction of two blending residual biomass. The main product is of co-torrefaction process is high quality bio-solid product.



Figure 6: Co-torrefaction Process.

#### **1.4 Problem statements**

Energy demand increases day by day, and the crisis of energy is one of the main issues in developing countries. An increase in the use and cost of non-renewable resources causes environmental pollution. Biomass is mainly disposed off by landfill or directly incinerated which causes environmental pollution and wastage of valuable energy resources. A lot of research work has been published on co-torrefaction of different type of lignocellulosic biomass and summarized in many review articles. Some review articles have focused on the use of advance techniques to revamp the quality of fuel [17][18]. The blending ratio is very important for co-torrefaction of rice husk and coffee bean ground. However, there is no comprehensive study on co-torrefaction behavior and evaluations of rice husk and coffee bean ground blend with different ration to the upgradation of fuel. To address scale up issues and process challenges in co-torrefaction process are needed to be address.

#### 1.5 Research objective

To overcome the existing challenges in co-pyrolysis by using agriculture feed, the current research explores the co-pyrolysis of rice husk or sugarcane bagasse mixed with sewage sludge in different proportions for production of useful products. The main research objective is to synthesize, characterize and explore performance of rice husk and coffee bean ground with different temperature of torrefaction. The following measurable objectives are considered in the present study.

- To upgrade the fuel characteristics of conventional biomass (rice husk) and nonconvention biomass(coffee bean ground) via co-torrefaction process and blending
- To check the impact of torrefaction temperature on fuel characteristics.
- To compare the coffee bean ground and rice husk from coal with the help of Venkrevelen diagram

#### 1.6 Scope of study

This research work is primarily puts emphases on the investigation of co-torrefaction of coffee bean ground and rice husk blends with different ratio to produce bio solids.

Coffee bean ground and Rice husk were collected from local market, Islamabad. To comprehend the properties of the coffee bean ground and rice husk, proximate and ultimate analysis was performed for essential information about the physicochemical properties of different blends.

Comparison of functional group existing in coffee bean ground, rice husk and their blends are characterized by Fourier Transform infrared spectroscopy.

The analysis of co-torrefaction also provides the complete profile of weight loss, torrefaction index at different torrefaction temperature. It also provides mass yield and energy yield during co-torrefaction process at specific conditions.

This study presents the thermodynamic investigation on co-pyrolysis of lignocellulosic biomass and sewage sludge blends by using Coats and Redfern method to understand the thermogravimetric data. Different reaction models are accessible to determine the thermodynamic parameters (enthalpy, Gibbs free energy and entropy) which have influence on pyrolysis behavior of different biomass and sewage sludge blends.

#### 1.7 Chapter Summary

This thesis comprises of five chapters. The exposure of each chapter is given in the following paragraphs.

- **Chapter 1** delivers vision of the subject, background and contemporary problems related to the work. It also clarifies the problem statement, research objectives and scope of the planned study.
- Chapter 2 will sketch the literature review achieved to describe the previous work done on the Co-torrefaction of different biomass and waste materials. It also includes review based on

parameters that effect the co torrefaction process, synergetic effect, types of co-torrefaction reactor, biomass type and its residue and application of Co-torrefaction.

- Chapter 3 covers the methodology related to the sample preparation, co-torrefaction investigation work presented in the research. It will also give the related information about experimental procedure and the main equipment contributing in the experimental investigations.
- Chapter 4 delivers results and discussions about material characterization, FTIR analysis of sample, mass yield, energy yield, proximate and ultimate analysis, and torrefaction index on yield base.
- **Chapter 5** reviews all the findings and conclusions in the current study and provides the future recommendations for the related work.

# **Chapter 2**

### **Literature Review**

#### 2.1 Introduction

The aim of this chapter is to critically review the co-torrefaction of different types of lignocellulose and non lignocellulose biomass. In addition, some critical discussions of co-torrefaction are also signified in this script. The discussion is based on the behavior of co-torrefaction parameters, its reactors and studies the collaborating effects of the blending of different feedstock's. People's in various counties rely on biomass as a sustainable energy source to meet expanding energy demands and support economic growth [10]. Most biomass is carbon neutral and low in sulfur, minimizing air pollution and greenhouse gas emissions[11]. In the opinion of most experts, today's development of renewable energy is essential for lowering the use of fossil fuels, greenhouse gas emissions, and pollution of the environment. Renewable biomass or bioenergy is the world's most plentiful energy source in these more modern technologies.

#### 2.2 Co-torrefaction of lignocellulose and non-lignocellulosic biomass

A typical pellet made from empty fruit bunch (EFBs) has carbon content around 45.50% with the calorific value of about 17.0 MJ/kg. which limit their use and economic viability[12]. Additionally, it contains a high amount of moisture and ash. It is possible to produce an energy-dense fuel that can be utilized as a co-firing fuel in power generation without the risk of slagging or fouling by using EFB torrefaction. The heating value can be increased significantly (26.2 MJ/kg) while the carbon content is significantly enhanced (up to 63.5%). Torrefied biomass can be integrated into coal-fired boilers via direct, indirect, or simultaneous co-firing systems. Co-torrefaction is a premixed biomass in which heat (200-300°C) is provide in the inert environment and used in direct co-firing systems that use between 10% and 50% torrefied biomass. Due to the larger biomass-to-coal ratio, the fuel has greater flexibility and produces less tar [13, 14].

It is possible to synthesis of bio-char from co-torrefaction of biomass, which can be utilized for co-firing or environmental remediation applications, through the thermochemical process of torrefaction. Using biomass for co-torrefaction with a low calorific value implies that the oxygen and carbon in the biomass are well distributed. Co-torrefaction can be employed to boost a fuel's calorific value. Numerous types of biomass waste can be used in this manner without any harm to

the environment. Bio-char, a high-quality solid fuel, and bio-oil can all be made by combining various types of biomass waste, thereby reducing waste disposal and greenhouse gas emissions [15]. Co-torrefaction of various feedstock enhance the fuel properties of product [15]. It is difficult to store hygroscopic raw biomass because of its higher moisture content and lower energy density. This means that the use of raw biomass as a fossil fuel alternative like coal is limited because of these features. Processing, on the other hand, can address the drawbacks of raw biomass. To achieve this, biomass can be pretreated by a process known as torrefaction. Temperatures of 200-300 °C are used in an inert or .nitrogen atmosphere during the heating of the raw biomass [16]. A previous study found that torrefaction can enhance the properties of biomass to a certain extent [1], such as reducing the raw biomass's moisture content, resulting in a rise in energy density and heating value [2]. Additionally, because raw biomass's hygroscopic characteristic has been inherently transformed to hydrophobic, co-torrefied fuel enjoys the advantages of a hydrophobic fuel properties [3].

The following table summarizes the most recent research on co-torrefaction of biomass and garbage, including studies, features, and outcomes. Co-torrefaction of biomass as a feedstock did not indicate a synergetic effect and the torrefied product displayed a insignificantly enhancement in the high heating value (HHV) for utilizing as a co-firing fuel [17]. Weight loss of 20–30 % of wet raw biomass is common during the torrefaction process. A co-torrefaction process used EFB pellets as the main feedstock and cooking oil (UCO) as a secondary feedstock to increase the calorific value and hence the quality of the EFB pellets. As a result, high-calorific-value torrefied pellets were produced that are more environmentally friendly. Microwave co-torrefaction (MCT) is a new technology that combines microwave heating with co-torrefaction. Torrefied biomass pellets were compared to typical furnace-based co-torrefaction in terms of their properties, manufacturing process, waste reduction, and energy conversion efficiency [18]. The study of the result show that to overcome the conventional heating microwave heating technology is the innovated technology integrated with torrefaction process [18, 19]. Work on co-torrefaction of various biomass and waste material is summaries in **Table 1**. Additionally, we discuss the process's variables, reactor type, and numerous analysis tools, including proximate and ultimate analysis, Van krevelan diagrams, and others. Impact of blending ratios and thermo-gravimetric measurements of mixing biomass are also discussed.

Sr.	Biomass	Blending	Process and Type	Process	Outcome	Ref
No.	type	ratio	of reactor	Condition		
1	Waste epoxy resin and fir	Mixing ratio of Fir: Waste epoxy resin is 1:3	Co-torrefaction Conventional heating batch-type reactor	Temperature: 120–180 °C Time: 10–40 min	Solid yield (%) 76.86 Enhancement of HHV 1.12 Energy Yield 85.79 Improved the evaporation of volatile compounds The solid yield was adversely affected.	[14]
2	Sewage	Mixing ratio	Co-torrefaction	Microwave	Biochar made	[19]
	sludge and	of Sewage	Microwave	power level	from pure	
	Leucaena	sludge:	heating	100W	Leucaena wood	
		Leucaena is		Time 30 min	has a CO <sub>2</sub>	
		75:25		Temperature170-	adsorption	
				390	capability of 53	
					mg/g.	
3	Biomass	Blending ratio	Vertical tubular	Temperature: 300	Produced mass	[20]
	and coal	of biomass:	furnace	°C Time: 60 min	yield: 57.0%	
		coal is 30:70			63.8% Energy	
					yield: 77.0–89.0	
					percent 18.1 – 22.2	
					percent reduction	
					in CO <sub>2</sub> emissions.	

 Table 1: Literature review of Co-torrefaction.

4	Microalgae		Co-Torrefaction	Temperature: 250	Better	[15]
	and	-		°C Time: 60 min	temperatures (92.6	
	Lignocellul		A gas		percent) resulted in	
	osic		chromatographic		a higher energy	
	Biomass		furnace with a		efficiency, but the	
			glass reactor		feed mixture's	
					moisture content	
					quickly diminished	
					this efficiency	
					(16.9 to 57.3	
					percent for 70	
					percent moisture).	
5	Mango seed	Blending with	Wet Co-	Temperature	Higher heating	[21]
	and passion	optoelectronic	torrefaction	from 120 to 180	value 19.0 MJ/kg •	
	shell with	sludge with		°C), reaction	92.1 energy yield	
	optoelectron	Mango seed at	Microwave reactor	duration from 10	There are fuel	
	ic sludge	a ratio of		to 40 min.	ratios of 1.60-1.82	
		25/75			and an energy	
					return on	
					investment of	
					14.7%.	
6	Food sludge	Blending	Wet co-	Temperature: 150	19.6 MJ/kg HHV;	[17]
	and	macadamia	torrefaction	°C duration: 20	decreased ash	
	lignocellulo	husk and		min	content; first-order	
	sic biowaste	sludge at a	Microwave reactor		kinetics; increased	
		25/75 ratio			thermal stability	
		(db%)			and combustion	
					efficiency of	
					biochar; 7.4 energy	
					return on	
					investment; 45.2	
					percent reduction	
					in carbon gas	
					emissions.	
7	Empty fruit	-	Co-torrefaction	Temperature:	There was 85.5 wt	
	bunch			200, 250 and 300	% mass yield •	
	pellet, used		Microwave reactor	°C. Heating rate:	Fuel ratio: 1.8 •	

	cooking oil,			5065 °C/min	Carbon content:	
	waste			Time: 5–8 min	68.3% • Fixed	
	engine oil				carbon:	
					62.3%•HHV: 28.0	
					MJ/kg.	
10	Hemicellulo	Weight ratio			• There was no	
	se,	(1:1:1)	Co-torrefaction	Temperature:	synergistic effect	
	cellulose,		Conventional	230, 260 and 290	from the co-	
	lignin,		heating Thermo-	°C.	torrefaction on the	
	xylan,		gravimetry.		weight loss of the	
	dextran,				blend.	
	xylose and					
	glucose					
11	Textile	-	Wet Co-	Temperature:	Amount of fixed	[17]
	sludge and		torrefaction	120–180 °C	carbon: 29.8% .	
	lignocellulo			Time: 10–30 min	HHV: 19.7 MJ/kg.	
	se bio-waste					
	(macadamia					
	husk)					

#### 2.3 Biomass residue and their properties

#### 2.3.1 Ultimate analysis

The ultimate analysis presents the compositional analysis into its constituent elements. The atomic ratio of hydrogen, oxygen, and carbon assists in comprehending the fuel heating value. Heating value of biomass depends on oxygen to carbon ratio (O/C) is very important as its decrease from 18.90 to 13.57 MJ/kg with an increase from 0.99 to 1.02 [21]. The oxygen, sulphur, and nitrogen content of Optoelectronic sludge (OS) and bio waste decreased while the carbon and hydrogen content increased because of the co-torrefaction process. Nitrogen (6.4 wt.%) and sulphur (4.6 wt%) were extremely low in the raw and torrefied products, which will lead to lower sulphur and nitrogen oxide emissions during burning. Carbon from bio-waste was more important than the value of HHVs in the environment. Biofuel characteristic are improved as a drop in oxygen content but an increase in hydrogen content, which increases stability and reduces the production of smoke (e.g. light volatile material) during combustion [22]. OS and bio-waste co-torrefaction resulted in

an increase in the release of hydrophilic functional groups, hence dehydrating the bio-char[23]. Additionally, during wet co-torrefaction, deoxygenation and decarboxylation reactions occurred [24]. Excess lignocellulosic material is expected to be degraded during torrefaction of EFB pellets, resulting in an incondensable bio-oil and an incondensable syngas. [18] . Increasing the temperature to 300°C resulted in a greater degree of devolatilization, resulting in higher carbon content of torrefied biomass pellets. [18]. The HHVs value of biomass were 14.8 MJ/kg for 0% lignocellulosic material (Lc) and 21.4 MJ/kg for 100% Lc, the lowest and highest values, respectively. Mixtures for co-torrefaction with Lc included at 0% to 50% , achieved HHVs greater than 18 MJ/kg at temperatures of 275 and 300°C. Chen et al [25] findings were approximately similar heating value when comparing bio-char's generated from sawdust, wheat straw, pine, and microalgae through torrefaction process. Nitrogen elimination and deoxygenation reactions have a substantial impact on the final qualities of the bio-char content, therefore bio-char's that underwent a co-torrefaction process at temperatures more than 275°C were shown to have improved fuel properties[26]. After co-torrefaction are given in **Table 2**.

Biomass/	Temp	Time	С	H	N	0	S	HHV	Ref
torrefied	(°C)	(min)						(MJ/kg)	
biomass									
Optoelectro			43.89	4.80	6.38	43.48	1.45	13.57	[21]
nic sludge									
(OS)									
Mangifera			46.11	5.54	0.89	47.20	0.27	18.90	[21]
indica seed									
(MIse)									
OS and	150	30	45.1	9.8	4.6	39.6	0.9	19.0	[21]
MIse									
(25/75) %									
Empty fruit			43	6	1.2	49.8	0	18.5	[18]
bunch (EFB)									
EFB pellet	300		68.2	8.0	0.7	23.1	0	26.4	[18]
with used									
cooking oil									

**Table 2**: Ultimate analysis of Biomass.

Cv			51.29	7.31 ±	9.05 ±	32.11	0.24	15.54	[15]
(Chlorella			± 0.09	0.42	0.00	±	±		
vulgaris)						0.10	0.04		
Lc			50.10 ±	6.21 ±	1.10 ±	42.59	0.00	18.94	[15]
(lignocellulo			0.16	0.09	0.08	±	±		
sic material)						0.04	0.00		
Lc	300	45	70.2	5.1	1.5	21.9	1.2	21.4	[15]
(lignocellulo									
sic material)									
100%									
Lc	300	30	61.2	6.0	5	27.6	0.2	19.1	[15]
(lignocellulo									
sic material)									
50%									

#### 2.3.2 Proximate Analysis

Reduced volatile matter (VM) and ash content resulted in an increase in the pellet's heating value and improved flame stability following co-torrefaction [18]. Bio-oil and incondensable syngas are projected to emerge from the decomposition of the lignocellulosic component of the EFB pellets during torrefaction, while the fixed carbon (FC) and carbon contents of ensuing torrefied biomass pellets increase [27]. Increasing the temperature to 300 °C resulted in a greater degree of devolatilization, resulting in torrefied biomass pellets with in higher carbon content[28].

The proximate compositions of bio-char were estimated, and their HHV values were utilized to establish their potential for energy or material applications. Initially the moisture content of EFB was 15%, and the HHV of 18.5 MJ/kg. The moisture level of EFB pellets containing used cooking oil is equal to 1, the HHV is 26.4 MJ/Kg<sup>-1</sup>, which is substantially more than the EFB alone [18]. The proximate compositions of samples of *Chlorella vulgaris* (Cv) and Lc differed significantly. The Cv had more ash, nitrogen, and volatile elements, whereas Lc included more fixed carbon and oxygen. Lc's reduced ash is related with a greater HHV, and its lower nitrogen content decreases the risk of detrimental NO<sub>x</sub> emissions during energy recovery [15]. Hybrid coal has low moisture content and a narrow range of 0.6 - 2.1% by w/w [20]. Dehydration breaks down some hydroxyl groups which hinder the establishment of hydrogen bonds, transforming hybrid coal into a hydrophobic substance[25].

Furthermore, the heat gained by the feed evaporated the moisture approximately 108°C, accompanied by the evaporation of volatile compounds at temperatures higher than 200°C [20]. Between 39.2-47.1 percent -w/w volatile matter as well as between 45.3 and 47.7 percent -w/w fixed carbon, hybrid coal has a wide range. During torrefaction, the biomass constituent, mainly hemicellulose, decomposes and will become free from a volatile matter [29]. Because of this, hybrid coal's volatile matter content is reduced while its fixed carbon content is increased. In terms of volatile matter, sugarcane bagasse biomass is most effective, followed by rubberwood but also empty palm fruit bunches [20]. Hybrid coals made from empty palm fruit bunches have the greatest ash content, followed by sugarcane bagasse and rubberwood. If you're going to use hybrid coals, you're going to have to use coal that isn't raw X coal. These variations in raw material ash content are consistent with these adjustments. During the process of torrefaction, ash remains fixed, causing this effect [30]. The variation in ultimate and proximate analysis of biomass before and after co-torrefaction are given in **Table 3**.

Biomass/	Temp	Time	Moisture	Volatile matter	Fixed carbon	Ref
torrefied	(°C)	(min)	Content			
biomass						
Optoelectro			99.00	64.89	9.30	[21]
nic sludge						
(OS)						
Mangifera			4.97	96.38	2.24	[21]
indica seed						
(MIse)						
OS and	150	30				[21]
MIse						
(25/75) %						
Empty fruit			15	62	15	[18]
bunch (EFB)						
EFB pellet	300		1	33	63	[18]
with used						
cooking oil						

**Table 3**: Proximate analysis of Biomass.

Cv			$6.35\pm0.52$	86.46	6.01	[15]
(Chlorella				$\pm 0.74$	$\pm 0.73$	
vulgaris)						
Lc			$9.28\pm0.84$	78.41	19.06	[15]
(lignocellulo				± 3.89	± 3.97	
sic material)						
Lc	300	45	5	58.6	34.9	[15]
(lignocellulo						
sic material)						
100%						
Lc	300	30	30	63.0	26.6	[15]
(lignocellulo						
sic material)						
50%						

#### 2.4 Synergistic effect

When two or more biomass wastes combine to generate an impact greater than either of them could produce alone, this is called a synergistic effect. By combining materials, synergistic effects may be used to increase co-torrefaction yields. Moreover, combining OS with MIse as well as PEsh for WT had a synergistic impact on increasing HHV contents in co-torrefied bio-char, especially at a 75/25 blending ratio [21]. As a consequence of these results, it is shown that combining OS with fruit bio-waste is an effective way further for enhancing the qualities of bio-char products and therefore is likely to be employed in place of traditional fuels in the future (e.g., coal) [31].

#### 2.5 Operation parameters

The co-torrefaction utilized a variety of biomasses that were thermo-chemically processed and acquired desirable qualities. During, co-torrefaction of biomass, numerous operating parameters affect co-torrefaction process such as temperature, residence duration, particle size, biomass type, and moisture content.

#### 2.5.1 Role of Temperature and Impact of Residence time on Mass and energy yield

The mass yield, energy yield, and energy density of torrefied biomass vary with temperature range as well as reaction time. The mass yield of OS decreased when the co-torrefaction temperature was raised from 120 to 180°C, from 98.4 percent after 10 min at 150°C to 79.9 % after 30 min at

180°C. Main constituents of raw sewage (such as low molecular weight hydrocarbons) degraded with increasing co-torrefaction intensity. This reaction had an energy density of 1.14 and a 100 percent energy yield at a co-torrefaction temperature of 150 °C and a reaction time of 30 minutes.[21]. The second highest energy yield of 99.4 percent was produced during co-torrefaction at a temperature as well as reaction time of 150°C and 10 min, respectively, with an associated energy density of 1.01. As a result, unnecessary energy consumption is reduced, and a high HHV of bio-char is obtained [21]. During the 20-minute torrefaction at 150°C, 95.2% of the energy was extracted, with a maximum energy density of 1.20 was attained.

Bio-char mass yield, energy yield, and energy density is affected by various blend ratios and types of bio-waste used [29]. OS and bio-waste co-torrefied together produced more than 80% of the total mass and energy. OS torrefied itself made mass and energy yields of 90.2 % and 100%, 91.7 percent and 93.9 percent for MIse, and 80.9 percent and 80.6 percent for PEsh. These are the same yields were reported for microwaves based torrefaction of OS, which may be due to the heating the interiors of samples at lower temperatures and for shorter periods of time, leading to their higher energy efficiency[32]. This might be because microwave irradiation heating modes are more energy efficient, since they can heat the interiors of materials at lower co-torrefaction temperatures also for shorter periods of time [33]. The bulk yields of bio-char decreased when the OS/bio-waste blending ratio was reduced from 75/25 to 25/75, especially in case of OS blending with PEsh. [21]. This phenomena might be explained by the fact that biomass has a larger microwave absorption capacity than sludge, resulting in significant devolatilization of biomass as the percentage of bio-waste in the blend increased [34]. Because MIse and PEsh have lower energy densities than pure OS, they increase the energy density of pure OS. When OS is combined using MIse and PEsh bio-waste, the energy and mass yields are the same. When the OS/bio-waste blending ratio was altered from 75/25 to 25/75, the bio-char mass yields decreased to some extend (95.1-92.1% for OS combined with MIse and 93.4-65.2% for OS blended with PEsh). These findings are consistent with the findings of another research that investigated the co-torrefaction of sewage sludge and Leucaena using microwave heating [33]. Note that when the OS-PEsh and OS-MIse co-torrefied bio-char was blended at 50/50 and 25/75, the mass and energy yields of the OS-PEsh co-torrefied bio-char were substantially lower than those of the OS-MIse co-torrefied bio-char [21]. Additionally, the paper notes that when bio-waste and sludge are mixed for cotorrefaction, the heat may degrade a significant amount of hemicellulose and cellulose, which

reduces the mass yield and energy yield of bio-char while retaining its greater energy content [34]. Additionally, bio-char made from 25% food sludge (FS) and 75% Macadamia husk (MH) on dry biomass basis, the highest energy density and yield, measuring 1.07 and 80.8 % was reported, respectively.

#### 2.5.2 Role of Temperature and Impact of Residence time on HHV

The quality of bio-char can be greatly influenced by the ratios of biomass used in the mixing process. Blending OS with MIse and PEsh bio-waste to generate bio-char with different HHVs. Mangifera indica seed (Mise) as well as Passiflora edulis shells (PEsh) bio-wastes were found to have experimental HHVs of 19.4 MJ/kg and 18.6 MJ/kg, respectively that were significantly bigger than OS (15.5 MJ/kg) after 30 minutes of torrefaction at 150 °C. Microwave-assisted WT was used to blend textile sludge and lignocellulose bio-waste, and the HHVs of bio-char increased in the same ratio as the blending ratios of the two types of bio-waste increased. After 30 minutes of torrefaction at 150°C, it was revealed that the maximum high heating values of OS mixed with MISE and PESH were both better than the values obtained with the other blending ratios (75/25 and 50/50%). These were 19.0 and 18.3 MJ/kg, respectively [21]. The resultant bio-char had a maximum of 19.2-21.1 MJ/kg of HHV, which was higher than that of lignite (18.7 MJ/kg) but equivalent to that of anthracite coal (19.2-21.1 MJ/kg) [35].. Fifty-five percent of the carbon in the bio-char was fixed carbon when compared to raw food sludge (FS). Bio-char's ash and fixed carbon contents were raised when FS and bio-waste were mixed together. As a result, agricultural biowaste can be properly disposed of by reusing it as renewable energy. As the blending ratio for biowaste increased, the HHVs more than FS was elevated, the heating values of the resulting bio-char increased as well. Sewage sludge and Leucaena co-torrefaction produced a similar outcome. When bio-char was made from torrefied food scraps, it had significantly higher HHVs than bio-char made from torrefied food scraps alone (19.2-20.04MJ/kg). With its high HHV content, FS with MH (25/75 db percent) showed the maximum amount of the experimental HHV [17].

This is consistent with those previously described for torrefied wood and agricultural biomass following hydrothermal carbonization [36]. Torrefaction higher degree of carbonization significantly accelerated the degradation of cellulose and hemicellulose, which resulted in a reduction in smoke (from fly ash, CO<sub>2</sub>, CO, NO<sub>x</sub>, and SO<sub>x</sub>) produced during biofuel combustion [37]. The increase in temperature of torrefaction and reaction time increases the HHV steadily.

The result has been shown that the reactor time of co-torrefaction is more affected than temperature for OS bio-char. The high heating value of bio-char is 24.1MJ/Kg at temperature of 300 °C at 45-minute residence time. The blended food sludge bio-char have obtain maximum heating value 18.9 MJ/kg at 150°C and 18.8 MJ/kg for 150°C at 30 min. The high heating value of food sludge bio-char is 21.7% more than raw sludge. [17]. Increased the temperature of torrefaction decreased the mass yield from 84.2%(120 °C for 30 minutes) to 67.7 percent (200 °C for 30 min), which could be attributed in part to protein and polysaccharide breakdown in the sludge solids [38].

#### 2.5.3 Van Krevelan diagram

Van Krevelan diagram was first used to categorize coals and estimate the compositional change throughout maturity by plotting atomic oxygen/carbon (O/C) against atomic hydrogen/carbon (H/C). Fuel quality is described using this term. In assisting us better understand a fuel's heating value, atomic ratio classification is useful for a variety of other purposes. Biomass's higher heating value (HHV), for example, ranged from roughly 20.5 MJ/kg to about 15 MJ/kg as the oxygen-to-carbon ratio rises from 0.86 to 1.03.[39]



#### Figure 7: Van Krevelen diagram.

The Ven krevelan diagram also describe comparison of the torrefied and Un-torrefied biomass. The torrefied biomass have more carbon content and less oxygen and hydrogen content as compared to Untorrefied biomass .The other aspect is that co-torrefied biomass have less Oxygen to carbon and Hydrogen to carbon ratio as compared to Untorrefied biomass shown in fig 3. This figure illustrate that untorrefied biomass such as OS 100%.Mise 100%,EFB 100%,Cv100%,Lc100% have low HHV due to its more O/C and H/C ratio and co-torrefied biomass such as OS25%+ MIse75%-Torrefied=150°C,EFB with used cooking oil-Torrefied=300°C,Lc 50%- Torrefied=300°C,Lc 100%- Torrefied=300°C have high HHV due to low O/C carbon ratio. The above discussion show that torrefied biomass has good quality fuel as compared to untorrefied biomass.

The Fig 7 also show that the O/C and H/C value of coal in which anthracite have very low value of O/C and H/C to show its high heating value. As we compare these values with biomass it has been shown that the biomass which have untorrefied faraway the coal value of O/C and H/C. On the other hand, the value of H/C and O/C for co-torrefied biomass have near to the coal value. For example EFB pellet with used cooking oil torrefied@T=300°C show that these value of O/C and H/C is very near to the anthracite coal which shown that this biomass have good quality of fuel. Fuel quality decreases when hydrogen-to-carbon and oxygen-to-carbon ratios increase. A decrease in the O/C ratio in comparison to the raw materials Cv and Lc was discovered in biochar formed at 200°C and 225°C, indicating some degree of deoxygenation, but no structural alterations were found because the H/C ratio was equivalent to the feedstocks. Thermal torrefaction results in biochar with O/C ratios equivalent to lignite and anthracite, further demonstrating the upgrading impact on fuel quality as the temperature rises [40]. A temperature-dependent decrease in the H/C ratio was also found at torrefaction temperatures greater than 250 °C, indicating that the carbonaceous structure is reorganized as more aromatic compounds are produced [41]. The lignocellulosic structure of bio-char undergoes enhanced rearrangement under high conditions of torrefaction, altering the material's porosity by eliminating the binding OH groups [42]. In comparison to raw biomasses, bio-char's also have a higher heating value due to their lower moisture content [43].

#### 2.5.4 Calorific value of different kinds of coal and biomass mixture

The calorific value of co-torrefied biomass is dependent on the oxygen, hydrogen and carbon content present in the feed. The feed contains more amount of oxygen and low amount of carbon content its calorific value is low, and vice versa. It is the primary objective of pretreatment to enhance the carbon concentration and reduce the oxygen level. Co-torrefaction is used to accomplish this. The oxygen concentration of biomass is the greatest of any fuel. As a result, it is difficult to turn biomass into liquid fuels because oxygen does not contribute to the heating value. Products can be made from biomass because of its high oxygen or hydrogen content. [39].Oxygen consumption in biomass reduces the amount of useful water produced by hydrogen, hence a high H/C percentage does not equate to a high gas yield [39].

#### 2.6 Reactor for Co-torrefaction technology

Numerous reactors configurations are reported for use in the co-torrefaction process are explained below.

#### 2.6.1 Conventional/ Fixed bed Reactor

The fixed bed reactor is frequently utilized in laboratory-scale torrefaction experiments used a fixed bed reactor in which biomass was dried and torrefied in a furnace before being used in their reactor. According to these authors, this is the most straightforward configuration of a reactor for biomass torrefaction [44]. At the conclusion of the process, the biomass is cooled and collected for further study.Su Shiung Lam et al.2019 study the co-torrefaction process in a muffle furnace with temperature controller enabled for regulation of heating rate at 10 °C/min for torrefaction of used cooking oil (UCO) pellets mixed with Empty fruit bunch (EFB). Temperatures were evenly distributed throughout the sample due to the high thermal conductivity of a covered graphite crucible (85.0 W/m-k). Each time, 50 g of pellets of EFB and 25.0 g of UCO were mixed together for 20 min at three different temperatures (200, 250, and 300 °C). UCO was not added to the EFB pellets that had been torrefied after that. All torrefaction studies were done twice to make sure they were the same [45].

#### 2.6.2 Fluidizing bed reactor

The Co-torrefaction process is also done in the fluidized bed reactor where biomass particles interact with gas stream. In co-torrefaction process multicomponent bed is selected for biomass

particles. For example, the particles of biomass and coal sludge using a multicomponent coal sludge and straw pellet bed. The fractional content of coal sludge varies as particle size distribution. The smallest particles accounted for 20.78 % of the total mass, whereas particles between 1.0 and 1.2 mm accounted for 61.79 %. Particles with a diameter of 1.5–1.7 mm accounted for 2.81 % of the total mass, whereas particles with a diameter of 1.7–2.0 mm accounted for 1.81% of the total mass. Particles with a diameter of 2.5 to 3.0 mm accounted for 0.47 % of the entire mass, whereas those with a diameter of 3.0 to 4.07 mm accounted for 4.07 % of the total mass. The sludge particles contained 5.35% moisture and had a density of 1680 kg/m<sup>3</sup>. The straw pellets averaged 6 mm in diameter and 12 mm in length and had a density of 1191 kg/m<sup>3</sup>. The "cold" model was tested using an acrylic glass column that allowed for visual examination and a piece of equipment measuring 485 mm in length, 194 mm in width, and 1500 mm in height. The column was supported by a perforated plate that served as an air distribution grille. Cooking took up just 5% of the grill's whole cross-section. A net was attached to the grill's top to prevent the mixture from clogging the holes. The device's air distribution grille was supported by a raschig ringequipped air suction chamber underneath the fluidized bed, which aided in the smoothing of the airflow. A blower with a pressure head of 4000 Pa was used to introduce ambient air into the fluidized bed. The highest flow rate measured was 1350 m<sup>3</sup>/h. Airflow control was performed via the use of a bypass conduit that bypassed airflow through a hose. The air velocity exiting the device was determined using a Delta-OHM HD 2103-1 hot-wire anemometer. Each experiment comprised at least 50 air velocity observations. The transition from a monodisperse to a fluidized state in a poly disperse particle bed is much different from that in a polydisperse particle bed, particularly when the particles have a variety of shapes and sizes [46-48]. The minimal fluidization velocity of a mixture of particles was hypothesized to be defined by a linear connection between the variance of the pressure difference between those and its mean value and thus the velocity of the gas blown over the bed. The **Fig 8** show the schematic diagram of a Fluidized Bed reactor system.



Figure 9: Fluidized Bed reactor [49].

#### 2.6.3 Microwave reactor

This reactor type is discussed using an example in which Cooking Oil (UCO) is combined with an empty fruit branch. This experiment utilizes a co-terrified and a microwave heating reactor. The same feedstock combination ratio was used three times without the use of a microwave absorbent in the MCT process (50 g of EFB pellet and 25 g of UCO). CO, CO<sub>2</sub>, CH<sub>4</sub>, and H<sub>2</sub> were released into the reactor, but they were kept there to keep oxygen from getting in and starting a fire. This created a low-oxygen environment that was ideal for torrefaction to happen. As shown in **Fig 9**, 1000 W of microwave power was used to conduct the MCT until the sample reached temperatures of 200, 250, and 300 °C. Microwave radiation was equally spread across the samples by maintaining the torrefaction process for a minute afterward. An Omega thermometer with a data logger attached to a K-type thermocouple was inserted into the sample through the reactor's top

aperture to record the torrefaction temperature. CCT-EFB stands for conventional co-torrefaction, while MCT-EFB stands for MCT with UCO. CT-EFB and MT-EFB, on the other hand, were derived through torrefaction without the use of UCO[45].



Figure 10: Microwave heat reactor [50].

#### 2.5.4 Production of bio-char via co-torrefaction in batch reactor

The co-torrefaction technique is used to produce bio-char in batch reactors. **Fig 10** is a schematic diagram of a batch-type reactor system. The entire system can be divided into three sections: the entrance, the main body, and the output. The in-take section comprised of a nitrogen gas cylinder (purity > 99 %) and a flow meter. The nitrogen flow rate was set at 100 mL/min. This system's primary body component was a glass tube. The study was conducted to enhance the bio-char's synergistic effect. The purpose of this study was to determine whether co-torrefaction with intermediate waste has a synergistic impact. Using epoxy resins and fir in a batch reactor to improve bio-char. The interaction was evaluated using the synergistic effect ratio.



Figure 11: Set-up of bio-char production through Co-torrefaction process[51]

A boat, a hook, and a furnace equipped with a K-type thermocouple assist in the separation of the two materials. Torrefaction ingredients were loaded into the boat. Materials weighing around 30 g were utilized for each run. In order to seal the glass tube, two plugs were used to secure the boat within. A hook was inserted into the plug to monitor the boat's whereabouts. In the furnace, a glass tube with a boat and a thermocouple attached to the sample pile's center was inserted and heated. Severe torrefaction was caused by the furnace's temperature being kept at 300 °C (Chen and Chen, 2020). Temperature surpassed 300 °C, and the timer started counting down at various time duration (20, 40 and 60 min) [52]. The accessory was used to draw the torrefied biomass (char) boat out of the glass tube when the torrefaction phase was completed. Weight percent char to raw biomass was used to figure out the solids output. Two cylinders and a cooling system were added in the system's output section. A water-coated glass tube was used to cool the device. A cooling water cycler delivered ice water (4 degrees Celsius) to the water coat. The liquid product of torrefaction was collected in the first cylinder after passing through the cooling system. Using mass balance, the liquid yield was calculated by dividing the liquid product by the starting material's weight. Following that, a water-filled cylinder was placed on top of the connecting pipe. Leak detection was carried out using this device. Nitrogen might get into the final cylinder, causing a lot of bubbles throughout the trials if the system wasn't adequately sealed. The nitrogen flow rate at the exit was monitored prior to the trials to assess the flow rate conservation.

#### **2.6** Application of co-torrefaction process

Co-torrefaction is employed for a variety of applications, including improving bio-char and CO<sub>2</sub> adsorption.

#### 2.6.1 Bio-char Enhancement

Although tar was formerly believed to be the primary source of energy in the liquid product, numerous experimental experiments have been published in the literature [53, 54]. It was treated as an undesirable result of torrefaction. Tar was chocking the facilities or pipes [55]. Its high viscosity was related to the existence of several heavy chemicals. Oil, on the other hand, lacked a significant HHV, but its lower viscosity made it easier to use in real-world applications [56, 57]. Tar, on the other hand, has a much higher HHV concentration than oil. Bio-char was coated with a new method of reusing tar in accordance with sustainability and circular economy principles, which improved its HHV. Tar was pipette-measured into charcoal at a volume of 0.5 ml followed by at least 12 hours of baking were required to verify that the enhanced bio-char had the same dry foundation as raw bio-char for the HHV measurement. Pre-modification and post-modification increase in the HHV. Furthermore, HHV of tar was the improved with ratio of Fir 60 to WE2 60 to Fir 40 to WE1 60 to Fir 20. To ensure that the two orders are similar, the coating procedure must be constant across all samples. Bio-char's increased porosity aided in the tar adsorption process over raw biomass [58]. This waste-to-energy approach, which used recycled tar to boost bio-char's HHV content, was an effective way to get rid of an unwanted byproduct while also treating it as a useful component.

#### 2.6.2 CO<sub>2</sub> adsorption through bio-char via the co-torrefaction method

Bio-char for  $CO_2$  adsorption was prepared using sewage sludge and leucanea wood by microwaveco-torrefied. Sludge to wood ratios of 75:25, 50:50, and 25:75 was used. Individual and mixed biomass samples were rendered inert at a microwave power of 250 W. Leucaena wood's carbon and fixed carbon content increased even if its mass also energy yields lessened. Carbon-rich biochar may be able to take up more  $CO_2$  molecules than lower carbon-rich bio-char. Adsorption capacity is about four times more for pure leucaena bio-char than for pure sewage bio-char. Increasing the amount of leucaena wood in the mix would have a negative impact on the bio-char's composition or characteristics, resulting in  $CO_2$  adsorption on bio-char. When it comes to  $CO_2$  adsorption on bio-char, it's possible that the adsorption reaction controls how well the intraparticle diffusion kinetic model performs [19].

 $CO_2$  adsorption increased at higher leucaena wood mixture concentration. Pure leucaena bio-char had around four times the adsorption capability of pure sewage bio-char. We estimated how much of each of the adsorbing qualities of pure sewage sludge as well as leucaena wood bio-char could be approximated at different combination ratios to get the theoretical values. According with findings, the observed  $CO_2$  adsorption capacity was close to the predicted value at 0.75 or 0.50. Unfortunately, the measured adsorption capacity was less than predicted for a mixing ratio of 0.25. [59]. Thus, the experimental result was lower than the theoretical prediction. Increased use of leucaena wood in bio-char may have a negative impact on its composition or characteristics, resulting in a diminished ability to absorb  $CO_2$ . To properly comprehend this occurrence, more investigation is required. Carbon-rich bio-char may be able to take up more  $CO_2$  molecules than lower carbon-rich bio-char. Pure bio-char made from leucaena wood had an adsorption capacity four times more than that of pure bio-char made from pine wood. There would be a negative impact on bio-char's composition or qualities due to an increased proportion of leucaena wood in the mix. When  $CO_2$  is adsorbed on bio-char, the procedure may have an impact on the  $CO_2$  adsorption rate [34].

# **Chapter 3**

### **Material and Methods**

#### 3.1 Materials and preparation

Coffee bean ground (CBG) was obtained from the I-8 Markaz Islamabad, Pakistan. The moisture content of the as-received CBG was approximately 85 wt%. Rice is the major crop of Pakistan and rice husk (RH) is collected a rice mill present in Hafizabad district present in Punjab Pakistan. The moisture content of the as-received RH was approximately 5-10 wt%. The feedstock has been pretreated and process for torrefaction. At the first step, received coffee bean ground and rice husk has been sun or air dried for one week and then dried in an oven at 105 degrees Celsius for one day to eliminate moisture content. Before applying to Co-torrefaction and relevant experiments, dried Coffee bean and Rice husk were grounded and shredded, into powder. Then it was sieved between 25 and 100 mesh to obtained the particle size in the range of (i 0.707–0.149 mm. The blended samples were obtained by mixing coffee bean ground and Rice husk at the ratios of 100:0,25:75, 50:50,75:25, and 0:100 named as CBG100%, CBG25%, CBG50%, and CBG75%, and RH100% respectively.

#### 3.2 Experimental setup

The co-torrefaction was instituted in the experimental setup as presented in **Fig 11**. The experimental system contain of a nitrogen cylinder as a source of nitrogen for non-oxidizing environment, Rotameter as a control valve, and a reactor. The control valve controlled the flow rate of nitrogen. The reactor comprised a quartz tube, a tube furnace, and a temperature controller. Samples were placed in the tube which was placed in the furnace. A digital temperature indicator (thermocouple) was mounted in the furnace beside the quartz tube to detect the temperature. The temperature controller was used to control the temperature inside the furnace. A conical flask was employed as the pass way and collected in a gas collection gas. Clean the exhaust gas stemming from Co-torrefaction.

#### 3.3 Experimental procedure and analyses

Tests were conducted on two distinct bio-waste types, including coffee bean grind and rice husk. A shredder and a vibrating screen were used to first shred and sift the garbage. To prepare the experimental samples, the sieved biomass was dried in a 105 °C oven for 24 hours. The samples were then put in sealed plastic bags. In each experiment, 3 g of sample was loaded into the quartz tube core. The tube furnace was initially heated to the necessary temperature for Co-torrefaction. The tube was then inserted into the furnace. While the sample was being torrefied, nitrogen at a flow rate of 50 mL min<sup>-1</sup> (25 °C) was constantly introduced into the reaction tube to provide an inert environment for the thermal breakdown of biomass and to eliminate volatiles released from the sample. So soon as the gas combination exited the tube, it was cooled and cleaned using waterfilled conical flasks to purify it.



Figure 12: Experimental setup of Co-torrefaction of rice husk and coffee beans ground.

Before conducting tests, the reaction system was nitrogen-leak tested to assure measurement accuracy. Typically, the experiment under each particular circumstance was conducted many times. The results of multiple runs were rather consistent, and the relative error was less than 5-10 percent. For the production of the data, the average values for each of the three trials were used. The properties of biomass before and after Co-torrefaction were thoroughly examined. The properties of the raw and Co-torrefied samples including Ultimate (Elementar Vario EL III),

Proximate analysis and Fourier transform infrared (PerkinElmer/Spectrum 100) analyses. The mass yield and energy yield was calculated by using the following equations [60].

$$Mass yield (\%) = \frac{mass of solid after torrefaction}{Mass of the sample}$$
(1)

$$Energy \ yield = \frac{Mass \ of \ torrified \ solid \times CV \ of \ a \ torrified \ solid}{mass \ of \ sample \times CV \ of \ a \ sample}$$
(2)

The torrefaction severity index is obtained by yield property-based. The WL,  $I_{torr}$ , and TSI indexes are based on physical properties measured on torrefied biomasses. The equations (**Eqs. (3**)– (6)) are summarized as

Weight loss (wt.%) 
$$WL = 100 - \left[\frac{w_{i(t)}}{w_o} \times 100\right]$$
 (3) [61]

Torrefaction severity index = 
$$TSI = \frac{100 - MY(t)_T}{100 - MY(60)_{300}}$$
 (4) [62]

 $Index of torrefaction = I_{torr} = \frac{HHV_{torrefied}}{HHV_{raw}}$ (5) [63]

Energy-mass co-benefit index 
$$(EMCI) = EY(t) - MY(t)$$
 (6) [64]

# **Chapter 4**

### **Results and Discussion**

#### 4.1 Mass Yield and Energy Yield

During torrefaction, the mass and energy yield are the two essential parameters that are examined. Fig 2 depicts the char MY at various temperatures (200 °C, 225 °C, 250 °C, 275 °C, and 300 °C) and blending ratios of CBG:RH (100:0%, 25:75%, 50:50%, 75:25%, and 0:100%. This particular trend depicts that mass of solid products decreases with an increase in the temperature, not only for the CBG but also for RH. A similar trend was noticed for the blending of CBG and RH due to little variation of mass yield. There is a little variation observed in CBG and RH as shown in Fig 2(c). The CBG peak decreases a bit at the temperature of 275 °C because of polymerized monosaccharides and also severe co-torrefaction conditions due to the intense reactions like dehydration, polymerization and depolymerization. This decrease in mass is related to the decomposition of stable component of biomass and volatile component degradation such as moisture and volatile matter [65]. Similar trends such as decrease in MY with the increase of temperature was also noticed for Oakwood, sewage sludge, and their blend in the already published article [66]. After blending, the highest MY (94.8%) is obtained at (200 °C) with a blending ratio of CBG:RH (50:50%), and the lowest MY was observed 61.4% at 300 °C with a blending ratio is CBG:RH (25:75%). The results depicts that the lower temperature favors the MY which is a good representation in term of energy saving.



**Figure 13**: (a) Effect of temperature on torrefied mass yield on various CBG-RH blends (b) Exposed representation of temperature (250 °C) effect on torrefied biomass yield (c) Exposed representation of temperature (275 °C) effect on torrefied biomass yield.

The energy yield (EY) shows the decreasing trend with the increase of temperature for RH, CBG, and the blending ratio of both feedstock's. Using **Eq. 2**, the EY was computed. **Fig. 3(a)** shows that the blending ratio of co-torrefied biomass CBG:RH (75:25%) at 200°C has a high EY (95.2%) and CBG:RH (25:75%) at 300°C have low EY (68.3%). Results of co-torrefied biomass of CBG 100% and RH 100% with a different blend of CBG:RH. EY of CBG 100% 200°C is (97.2%) that express maximum value. **Fig. 3(b)** indicate result of co-torrefied biomass and its temperature 200°C and 225°C but at 250°C there is slight variation is present in CBG:RH (75:25%) that is presented in **Fig 3(c)**. The EY is directly related to the CV of co-torrefied biomass, so the EY will be high with high CV value. The CV and the MY of the co-torrefied biomass are the two main factors that increase or decrease the value of EY. Because the rise in reaction temperature was beneficial to increasing the energy density of torrefied sample.



**Figure 14**: Impact of temperature on energy yield of torrefied biomass yield (b) Exposed representation of temperature (225 °C) effect on torrefied energy yield (c) Exposed representation of temperature (250 °C) effect on torrefied energy yield.

#### 4.2 Ultimate and Proximate Analysis

The ultimate analysis is used to determine the element composition (carbon, hydrogen, nitrogen, sulphur and oxygen) and proximate analysis is used to determine the ash content, fixed carbon and volatile matter of torrefied biomass at different temperature of (200°C, 225°C, 250°C, 275°C, 300°C) with different blending ratio (100:0, 25:75, 50:50, 75:25, and 0:100 named as CBG100%, CBG25%, CBG50%, and CBG75%, and RH100%) .The results of proximate and ultimate analyses are given in **Fig 14** and **Fig 15**. The result indicates that degradation of rice husk, coffee bean ground, and their blending ratio starts with an increase in the temperature. The ultimate analysis shows that increasing the temperature increases the carbon content and decreases the oxygen content is due to the removal of volatile matter and moisture content that is mostly contain of oxygen content [66, 67]. The **Fig.14** shows that high carbon content of 55.32% and low oxygen content of 24.81% was obtained at 300 °C after blending the rice husk and coffee bean ground

with a blending ratio 75:25, respectively. The result also indicates that low carbon content is obtained as after blending the rice husk and coffee bean ground is 48.21% and

high oxygen content 31.24% at 200°C with blending ratio is CBG: RH (25:75). By comparing this with 100%CBG and RH, the resulting state that CBG100% have maximum carbon content of 65.28%. Coffee grounds contain lipids that are higher molecular weight compound containing multiple carbon bonds. O content is higher when the CBG 5 is higher in the blending mixture is due to the higher O content in in RH as indicated in **Fig 15**.



Figure 15: Impact of temperture on ultimate analysis of co-torrefied feedstock.

The result of the proximate analysis shows that the volatile matter decreased with increased of temperature is due to the loss of Hydroxyl group (-OH) and the degradation of hemicellulose fraction of bio wastes [68, 69]. The maximum fixed carbon content obtained after blending the rice husk and coffee bean ground is 24.45 at 300°C with a blending ratio is CBG: RH (25:75) and 14.98% at (200°C) with a blending ratio CBG: RH (50:50). The maximum volatile matter (79.05%)

is obtained at (200°C) with blending ratio CBG: RH (50:50 and minimum (42.79%) at 300°C with blending ratio is CBG: RH (25:75). The presented data of volatile matter is varied with the mixing ratio of CBG and RH which shows that the targeted VM can be obtained for a particular application.



Figure 16: Impact of temperture on proximate analysis of co-torrefied feedstock.

#### 4.3 Ven Krevelen Diagram

The conversion of biomass feedstock into energy is possible when its properties approaches to the coal which is identified by Ven Krevelen Diagram [67]. The significantly raise in torrefaction temperature, the elemental carbon content of torrefied biomass tends to increase, while oxygen and hydrogen portions decrease caused by the release of volatile being rich in hydrogen and oxygen, such as water and CO<sub>2</sub>, which leads to decreased H/C and O/C ratios and creates the fuel blends shift towards coal. **Fig 16** illustrates the coal, torrefied and co-torrefied biomass (coffee bean ground: rice husk) in the Van Krevelen diagram (coffee bean ground: Rice husk). It is possible to gasify and co-fire biomass by co-torrefaction, which transforms its chemical composition and fuel qualities from biomass to peat, lignite, and even sub-bituminous [69].



Figure 17: Ven krevalen Diagram for H/C and O/C ratio for CBG, RH and their blends.

The result shows that RH 100% and CBH: RH (25:75)% at 200°C have high O/C and H/C atomic ratios, which shows its fuel property is not good. On the other hand, CBG100% and CBH: RH (75:25)% at 300°C show low O/C and H/C atomic ratios, which show good bio-solid fuel properties. As we compare these with coal, CBG 100%, and CBH: RH (75:25)% at 300°C resemble more and high heating value than coal. The effect of temperature shows that high temperature makes the chemical compositions of torrefied biomass more accessible to coal. The sequence of high fuel Properties is as follows.

Anthracite Coal >CBG 100% (300°C) > CBH: RH (75:25) % (300°C).

#### **4.4** Fourier transform infrared spectrometer (FTIR)

FTIR analysis to determine the functional group present on the surface of torrefied biomass. This technique analyzes the chemical changes of torrefied coffee bean groun100%, co-torrified rice husk 100%, blending ratio of coffee bean ground and rice husk 50:50.25:75,75:25) at temperature 300°C. The FTIR spectra of the torrefied rice husk, coffee bean ground and their blended ratio are

provided in Figure. To explain some important structural changes, some well-defined peaks were labeled and assigned to different functional groups as follow. (a) CBG 100% at 300°C show three wavelength 3429.35 contain 0-H bond [70],2923.36cm<sup>-1</sup> [71] contain alkane (C-H) and near 1631– 1637 cm<sup>-1</sup> is the bending vibration peak of N-H amide [70].(b) RH 100% at 300°C show four wavelength in which 3416.70 cm<sup>-1</sup> which is caused by the stretching vibration of (0-H bond) [70] , 2922.40 cm<sup>-1</sup> contain alkane (C-H) stretching in lignin as a functional group [72], 2852.26 cm<sup>-1</sup> <sup>1</sup> contain C-H stretching vibration of the aliphatic band [73], Simultaneously, the stretching band of the benzene ring shifted from 1597  $\text{cm}^{-1}$  to 1627.53  $\text{cm}^{-1}$  [74] .c) CBG:RH (50:50) at 300°C show four wavelength 3433.51 cm<sup>-1</sup> contain functional group alcohol as 0-H bond [75], 2922.42 cm<sup>-1</sup> <sup>1</sup> were ascribed to -CH<sub>2</sub> symmetric and asymmetric stretching vibration [76], and 1631.99 cm<sup>-</sup> <sup>1</sup>containg mainly characterized aromatic bonds (e.g., C-H, C=C, C=O) [77].and 1107.02 contain halogen C-F.(d) CBG:RH (25:75) at 300°C show three wavelength 3431 cm<sup>-1</sup> for O-H bond vibration ,2923.29 cm<sup>-1</sup> contain aliphatic –CH<sub>2</sub> [78] and the FTIR intensity of –NH at 1626.61 cm<sup>-1</sup> <sup>1</sup> [79].e) CBG:RH (75:25) at300°C show three wavelength 3420.06 cm<sup>-1</sup> for the vibration of 0-H bond [80],2923.76cm<sup>-1</sup> attributed to aliphatic -CH<sub>2</sub> [78]stretching and 1432.98 cm<sup>-1</sup> CO (1652-1725 cm-1) [81] ,1115.1 cm<sup>-1</sup> assigned to alcoholic C–O stretching vibration [82]. The O-H group represent the presence of hydroxyl, carboxylic acid. The intensity of different peaks shown in the figure having shown different functional such as alkane, alkene, carboxylic acid, aldehydic group, alcohol and phenol.



Figure 18: (a) CBG100% (b) RH100% (C) CBG: RH (50:50) (d) CBG: RH (25:75) (e) CBG: RH (75:25) at 300°C.

#### **3.4** Severity index

The severity index is used to determine the extent of biomass degradation during torrefaction [83]. The formula of torrefaction indexes such as weight loss, torrefaction severity index, and torrefaction index on the basis of yield is determined by **eq (3-5)**. Commonly, weight loss is the first metric employed while calculating the torrefaction severity index. The result indicates that higher co-torrefaction temperature cause increased degradation, and the result is high weight loss. The blending ratio of CBG: RH (25:75) at 300 °C shows a maximum weight loss of 38.6%, and the blending ratio of CBG:RH (50:50) at 200 °C has a minimum weight loss of 5.2%. The weight loss of torrefied biomass before blending reveals that the minimum weight loss of CBG 100% is 4.9% at 200 °C and RH100% has a maximum weight loss of 40.1% at 300 °C.

Biomass	Temp (°c)	WI	TSI	Torrefaction index	EMCI
		(%)			
CBG 100%	200	4.9	0.133152	1.022082019	0.021
CBG 100%	225	7.7	0.209239	1.030335861	0.028
CBG 100%	250	11.7	0.317935	1.073612684	0.065
CBG 100%	275	26.5	0.720109	1.217687075	0.16
CBG 100%	300	36.8	1	1.332278481	0.21
RH 100%	200	8.8	0.219451	1.031798246	0.029
RH 100%	225	11.8	0.294264	1.052154195	0.046
RH 100%	250	15.7	0.391521	1.071174377	0.06
RH 100%	275	27.02	0.673815	1.074266922	0.0542
RH 100%	300	40.1	1	1.133555927	0.08
CBG: RH(50:50)	200	5.2	0.158055	1.004219409	0.004
CBG: RH(50:50)	225	10.8	0.328267	1.047085202	0.042
CBG: RH(50:50)	250	14.1	0.428571	1.074505239	0.064
CBG: RH(50:50)	275	24.1	0.732523	1.065876153	0.05
CBG: RH(50:50)	300	32.9	1	1.084947839	0.057
CBG: RH(75:25)	200	6.8	0.195402	1.021459227	0.02
CBG: RH(75:25)	225	8.8	0.252874	1.028508772	0.026
CBG: RH(75:25)	250	13.2	0.37931	1.059331797	0.0515
CBG: RH(75:25)	275	21.9	0.62931	1.039692702	0.031
CBG: RH(75:25)	300	34.8	1	1.153527607	0.1001
CBG: RH(25:75)	200	8.4	0.217617	1.027510917	0.0252
CBG: RH(25:75)	225	10.9	0.282383	1.046015713	0.041
CBG: RH(25:75)	250	15.2	0.393782	1.076650943	0.065
CBG: RH(25:75)	275	27.52	0.712953	1.088576159	0.0642
CBG: RH(25:75)	300	38.6	1	1.11237785	0.069

**Table 4**: Yield base torrefaction index for RH, CBG and their blends.

The torrefaction severity index (TSI) is another parameter that normally lies between 0 and 1. TSI is a dimensionless parameter which is normally evaluating the energy performance. Table 1 also shows that increasing the temperature increase the TSI and at 300°C value reaches 1. The Torrefaction index is the third parameter which is the ratio of torrefied HHV to raw HHV. The measured value of blending and non-blending Co-torrefied biomass is shown in Table 1. The result

also indicates the energy-mass co-benefit index (EMCI); EMCI is the difference between solid and energy yield, which formula is shown in equation 6, and the value of this index is shown in table 1. The result tells us to increase the co-torrefied temperature to higher the EMCI value.

### Conclusion

The potential for biomass blends of various intermediary bio-wastes to be used as alternative fuels According to the outcomes of the Co-torrefaction experiment, the consequence of Co-torrefaction had no effect on biomass that suffered severe torrefaction and lost weight. On average, the effect of co-torrefaction on lignocellulosic biomass was the most pronounced, as a result of hemicellulose and cellulose evaporation. Bio-char made from co-torrefied bio-waste is a good contender for energy generation in place of coal. Concerning the final compositions, the bio-char was deoxygenated, decarboxylated, and dehydrated during co-torrefied samples. The sophisticated HHV, fixed carbon content, and energy density were found in bio-char generated from feedstocks that were torrefied only or in relation to different blending ratios. As a result, co-torrefaction provides an option for the conversion of bio-waste into biofuel with high efficiency. Consequently, it is considered a promising procedure for the production of high-quality biofuel that can serve as an alternative to the disposal of bio-waste while reducing concerns with the waste disposal. The result of co-torrefaction of coffee-bean ground (CBG) and rice husk (RH) shows that mass yield and energy yield is depend on temperature. The mass yield and energy yield of different blend ratios decreased with enhanced temperature. The ultimate and proximate analysis of the blending ratio of CBG and RH indicates that increasing temperature decreases the volatile matter, and oxygen content and carbon content increase due to increased heating value. The optimum blending ratio CBG: RH (75:25) of that high carbon content obtained after blending the rice husk and coffee bean ground is 55.32%, and the low oxygen content is 24.81% at 300°C. High carbon content and low oxygen content show good solid biomass. The Co-torrefaction process involves the decomposition of hemicellulose and partial depolymerization of lignin and cellulose. The result of FTIR also showed the functional group present on the surface, such as (alkane, alkene, carboxylic acid, aldehydic group, alcohol, and phenol) co-torrefied biomass. The Ven Krevalen diagram shows that CBG 100% and CBH: RH (75:25) % at 300 °C show the optimum result as compared to another co-torrefied biomass. The Co-torrefaction severity index increases with increasing temperature, and degradation result also enhance the weight loss with increasing Co-torrefied temperature, energy-mass co-benefit index.

# **Future Recommendations**

It's not like all aspects of Co-torrefaction and its impact on several other processing steps have been investigated. Future research objectives may include the following:

- Co-torrefaction techniques depending on activation energies necessary for degradation of cellulose, hemicelluloses, and lignin.
- Co-torrefaction may be examined at the microscopic level by identifying unique functional groups as well as the energy required to cleave bonding bonds.
- Utilizing Fourier transform infrared (FTIR) as well as Raman spectroscopy to study the spontaneous co-torrefaction process.
- By using Hunter colorimeter, determine the level of co-torrefaction severity predicated on changes in color.
- > Thermo gravimetric analysis was utilized to investigate the kinetics of weight reduction.
- > Investigating how various temperatures affect the structure of biomass.
- > Integrating torrefaction and densification as part of an integrated operation.

➤ A method for calculating the amount of energy required for the production of both condensable and non-condensable products via torrefaction.

Addressing the off-gassing as well as spontaneous combustion behaviour of torrefied biomass stored at various storage temperatures.

The recommendation process of co-torrefaction process

➢ If you're interested in generating ecologically friendly fuels, it's essential to comprehend the environmental aspects of alternative fuel techniques.

➢ It is possible to considerably reduce emissions by increasing the biomass fuel's properties. Consequently, biomass must be processed before being used in energy applications to optimize its fuel properties. It's essential to consider the environmental impact of the pretreatment procedures because they use vast amounts of energy and other resources.

➤ When determining whether a bioenergy system is environmentally feasible, the most often used method is life cycle analysis (LCA).

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