



MICROWAVE PYROLYSIS OF DEFATTED RICE BRAN FOR THE PRODUCTION OF INTERMEDIATE PLATFORM CHEMICAL (2-FURANMETHANOL) AND SYNTHESIS OF VALUE ADDED CHEMICALS

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ABSTRACT

2-Furanmethanol is a significant Chemical intermediate compound synthesized from Defatted rice bran (DRB) under microwave irradiation. Defatted rice bran (DRB) feedstock produced as a byproduct after extraction of Rice Bran oil by rice milling method. This plays a vital application for the production of fuels and chemicals due to rich content of lignocellulosic material. Our study reveals that the process is energy efficient and cost effective conversion of DRB into value added chemicals via platform chemical intermediate through aldol condensation reaction in presence of initiator under microwave irradiation. The synthesized material was well characterized by FT-IR, UV-Visible spectra, GC-MS analysis that confirmed the presence of various value added chemicals.

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INTRODUCTION

The production of fuels from biomass resources is widely accepted as a sustainable alternative to petroleum-derived fuels, which fulfills the increasing energy demand of the present scenario¹. In present state of affairs the fossil resources supply approximately 86% of energy and 96% of organic chemicals, in due course of time it is evident availability of non-renewable petroleum chemicals will be increasingly inaccessible to meet the growing needs of car-based society. Due to the green house gas emissions from transportation and other environmental impacts are demanding promising renewable biomass resource as alternative which can provide energy and chemical feedstocks that are suitable for the present and next generation.

Mankind must move towards renewable, alternative, sustainable, efficient and cost-effective energy sources with lesser emissions to produce liquid fuels and high value products via sustainable processes²⁻⁴. Need to establish sustainable energy technology is most important and urgent global issue in the present scenario. With advances in conversion technology, plentiful biomass resources have the potential to regain their central position as feedstocks for civilization, particularly as renewable carbon sources for transportation fuels and chemicals⁵.

Among abundant biomass resources rice bran offers significant potential as an alternative low-cost feedstock for biofuel and value added chemical production as it is a low-value co-product of rice milling; which contains approximately 15-23% oil. Only a small portion (< 10%) of rice bran is currently processed into edible rice bran oil (RBO) due to problems with instability from which biodiesel is produced⁶⁻⁸. The residue left after extraction of rice bran oil is known as defatted rice bran (DRB). Presently DRB are used as source of fertilizers, fuel for thermal plants in the form of briquettes, a portion of the DRB is used as animal feeds, mushroom production, gasification and around 30% of DRB is unused. This unused DRB can be used as the main raw material for the production of biofuels, intermediate chemicals and value added products. There are already a considerable range of chemical building blocks derived from renewable resources⁹.

DRB is one of the lignocellulosic biomass which is obtained from low-value high volume agricultural biomass typically edible plant material, including dedicated crops of wood and grass, and agro-forest residues¹⁰. Lignocelluloses are mainly composed of cellulose, hemicellulose, and lignin. Among them, the major component of lignocellulosic biomass is cellulose. Cellulose is a homopolysaccharide composed of anhydro-D-glucopyranose units, linked by β -1,4-glycosidic bonds¹¹. Cellulose is considered to be the strongest potential candidate for the substitution of petroleum-based polymers owing to its eco-friendly properties like renewability, biocompatibility and bio-degradability¹². By acid hydrolysis processes cellulose can be efficiently converted to monomeric sugars and can play an important role to meet future energy

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needs¹³. Thus, it is a promising alternative to limit crude oil, which can be utilized to produce biofuels, biomolecules and biomaterials¹⁴.

Currently biodiesel and bioethanol are most widely used biofuels obtained by trans esterification of triglycerides with ethanol while bioethanol is mainly obtained from edible/non-edible biomass sources such as sugarcane or corn by sugar fermentation processes. These biofuels are slightly corrosive in nature, low oxidation stability, increasing the risk of engine damage. So these limitations have motivated the search for new approaches to the production of high energy density biofuel (advanced biofuels) compatible with the present infrastructure. Many different conversion strategies like aldol condensation, acetylation, etherification, hydrogenation reactions etc., are used for the catalytic upgrading of platform molecules like furfural and HMF, which are two key chemical building blocks from lignocellulosic biomass for the production of transportation fuels as well as useful value added products¹⁵.

Most of the chemical processes were performed at elevated temperature under conventional heating systems such as an oil-bath for hours. In contrast, it has been widely recognized that microwave irradiation has potential to improve organic reaction efficiency. Microwave-assisted synthesis has received increasing attention in recent years as a valuable alternative to the use of conductive heating for accelerating chemical reactions. With no direct contact between the chemical reactants and the energy source, microwave-assisted chemistry is energy efficient, provides fast heating rates, increased product yield, improved selectivity and higher bulk operating temperatures and enables rapid optimization of procedures¹⁶. Hence this work aims to attain the principles of Green chemistry for the sustainable development which meets the needs of the present generation without compromising the ability of future generations to meet their own needs and also green chemistry efficiently utilizes renewable raw materials, eliminate wastes and avoid the use of toxic and or hazardous solvents and reagents in both product and processes in order to achieve the green chemistry principles. In this present work, the aldol condensation reaction has been chosen as one of the synthetic strategies for the production of transportation fuels and chemical intermediates by microwave pyrolysis.

Experimental section

Raw materials and chemicals

Rice bran was purchased from a local rice mill, Bangalore. The chemicals such as conc. HCl, acetone and hydrogen peroxide were purchased from S D Fine Chemicals Ltd, Bangalore and used without further purification.

Defatted rice bran preparation

Defatted rice bran obtained by soxhlet extraction with acetone. The mixture was refluxed for 8 hours at 55-60°C. The residue left after extracting rice bran oil was dried overnight and preserved for further analysis. The extraction procedure was repeated batch wise.

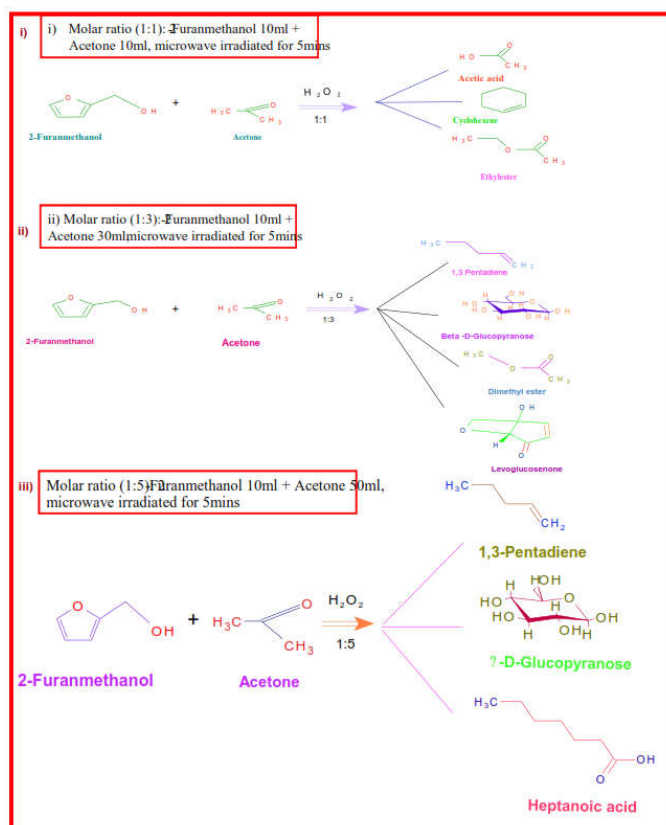
Acid hydrolysis of the DRB

The acid hydrolysis of the DRB was carried out batch wise using Conc.HCl and 500ml distilled water in round bottom flask. Reflux the reaction mixture for 8 hours at 55-60°C. Reaction mixture was filtered using Buckner filtration unit.

The obtained filtrate (dark brownish liquid) indicates the presence of 2-furanmethanol intermediate compound and it forms the starting material for the production of value added chemicals and transportation fuels using various synthetic strategies. The filtrate of defatted rice bran (FDRB) was collected and subjected to characterization. Further the residue left after filtration was dried in a hot air oven and its weight is determined and preserved for further analysis. The FDRB sample was characterized by GC-MS, FT-IR and UV-Visible spectroscopy (Fig.1-2).

Aldol-Condensation reactions via 2-furanmethanol intermediate using DRB filtrate

2-Furanmethanol acts as a renewable platform chemical and has wide applications in the field of condensation reaction, polymerization, production of transportation fuel etc. Aldol condensation reaction was one of the synthetic strategies used to obtain value added chemicals carried out by refluxing different molar ratios of 1:1, 1:3, 1:5 filtrate and acetone respectively in presence of hydrogen peroxide initiator (scheme-1).



The reaction mixtures were microwave irradiated for 5mins, cooled for 1hour. The aldol products were characterized using GC-MS, UV-Visible and FT-IR spectroscopy (Fig.3-6).

RESULTS AND DISCUSSIONS

Characterization of the filtrate (FDRB)

The filtrate was well characterized using Gas chromatography-Mass spectroscopy, Fourier transform infrared (FT-IR) spectra of the sample was then recorded in the range 4000-400cm⁻¹ using Spectrum Two model PerkinElmer FT-IR spectrophotometer having resolution of 4cm⁻¹ fitted with a LiTaO₃ detector. The UV-Visible study of the sample was

performed in the range 190-950nm using UV-VIS system-cary 8454, Agilent Ttechnologies. All this characterization of the filtrate confirms the presence of 2-furanmethanol compound.

GC-MS Spectral Analysis

The Fig.1 (a) and (b) shows the GC-MS spectra of the FDRB, the maximum peak in the graph indicates the relative abundance of 2-furanmethanol compound. The presence of 2-furanmethanol compound is also confirmed by FT-IR spectra and UV-Visible spectra.

FT-IR Spectral Analysis

The Fig.2 (a) shows the FT-IR spectra of FDRB indicates the presence of various functional groups present in the DRB filtrate. The strong broad absorption band at 3369cm⁻¹ and 3592cm⁻¹ indicates the stretching vibration of the hydroxyl groups. The absorption bands at 1049cm⁻¹, 1153 cm⁻¹ and 1414cm⁻¹ attributed to C-O stretching vibrations confirms the presence of esters. The absorption bands at 1634cm⁻¹ indicates the presence of alkenes. The absorption bands at 1725cm⁻¹ indicates the stretching vibrations of carbonyl, carboxylic acid and aldehyde groups. The absorption band at 2103cm⁻¹ is attributed to alkyne, the absorption band at 2942cm⁻¹ is attributed to stretching vibrations of C-H bond and also the vibrations in the range 1,650cm⁻¹ to 2,000cm⁻¹ confirms the presence of conjugation and the detailed values are given in Table.1.

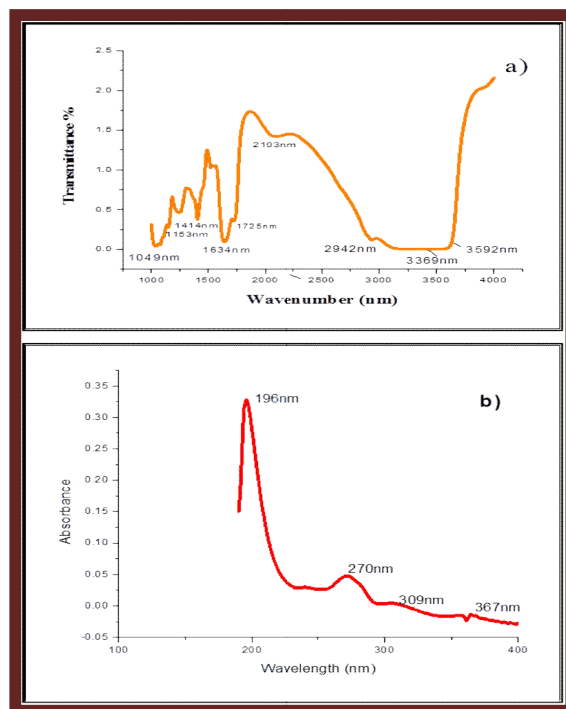


Figure 2a) FT-IR absorption bands for the functional groups present in FDRB and (b) UV-Visible spectra of FDRB.

UV-Visible Spectral Analysis

The Fig.2(b) shows UV-Visible spectra for the FDRB in which the major peaks with maximum absorbance (λ_{max}) at 196nm attributes for the presence of acids, esters, the minor peak at 270nm attributes for the presence of carboxylic acids, aldehydes/ketones carbonyl groups, dienes and alcohols and also absorbance peak at 309nm shows the presence of lignoglucoside. This indicates many value added chemicals are synthesized by aldol condensation reaction.

Characterization of synthesized aldol products from 2-Furanmethanol

GC-MS analysis

The Fig.3 shows the relative yield of the aldol products for 1:1 ratio indicates the presence of products such as acetic acid, ethyl ester, 2-(2-buten-1-yl)-2-nitro-, cyclohexene, 1,2-dimethyl-1-methylcycloheptene appears as minor peaks. The Fig.4 shows the aldol products for 1:3 ratio indicates the presence of products such as 1H Indene-2-phenyl, N-CycloOct-4-enylacetamide, 2, 4, 6-Octatrienal appears as major peaks and minor peaks as β -D-Glucopyranose, 1,6-anhydro- β -D-glucofuranose etc.

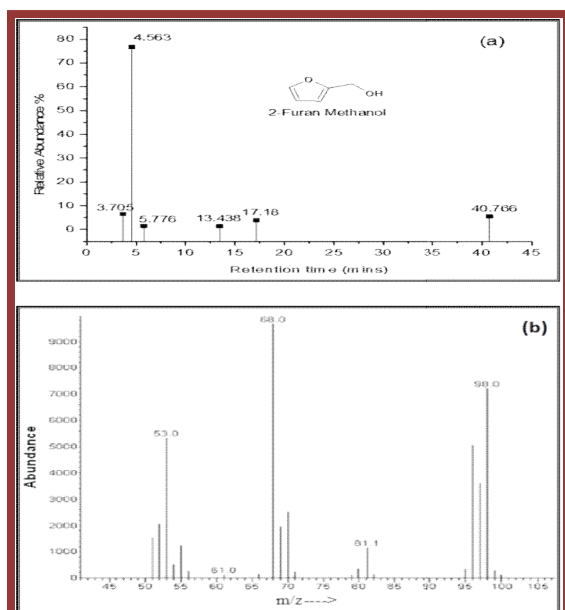


Figure 1(a) Plot of relative abundance against retention time for FDRB and (b) GC-MS chromatogram for the FDRB.

Table 1 FTIR absorption bands for functional groups present in 2-Furanmethanol.

Sl. No.	Types of vibration	Wave number (cm ⁻¹)
1	OH broad band	3369-3592
2	C-H stretching band (Alkane)	2934
3	C=O	1725
4	C-O vibration	1049-1414
5	C-H stretching band (Aromatic rings)	3010-3100
6	Conjugation (Alkene and alkyne)	1650- 2100

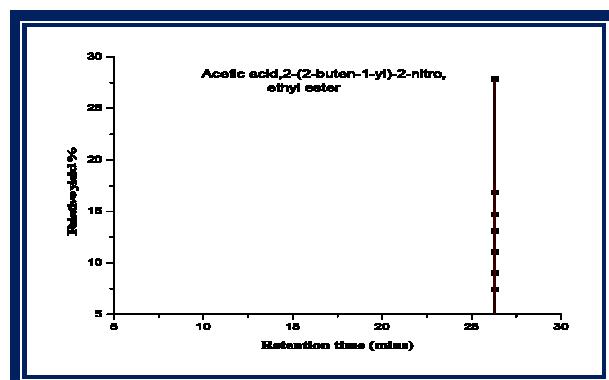


Figure 3 GC-MS plot of relative yield against retention time for 1:1 ratio

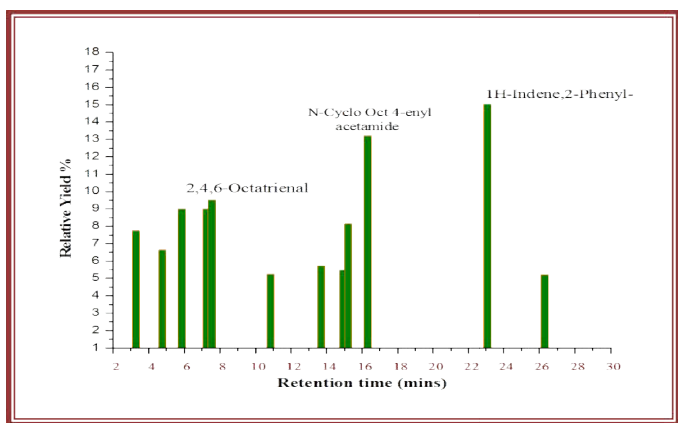


Figure 4 GC-MS plot of relative yield against retention time for 1:3 ratios

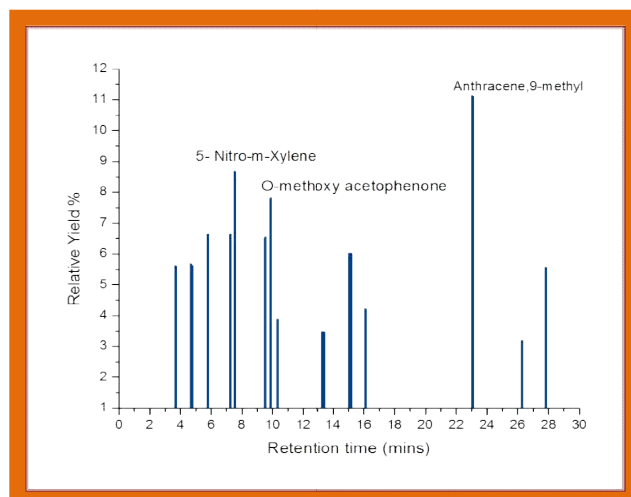


Figure 5 GC-MS plot of relative yield against retention time for 1:5 ratios

The Fig.5 shows the relative yield of the aldol products for 1:5 ratio indicates the presence of products such as 5-Nitro-m-xylene, O-methoxy acetophenone, Anthracene, 9-methyl appears as major peaks and minor peaks as heptanoic acid, 1, trans-β-D-glucopyranose, 5-ethyl-2,4-dimethyl compounds etc. Hence the GC-MS spectral studies for 1:1, 1:3 and 1:5 ratios indicates the presence of carboxylic acids like acetic acid, heptanoic acid, esters, aldehydes, dienes, amides, ketones, alcohols, cycloalkanes etc are the value added chemicals obtained from aldol condensation reaction by microwave pyrolysis as shown in Table.2.

Table 2: Shows the retention time and relative yield for all the three ratios of samples:

1:1 ratios: 10ml filtrate+10ml Acetone+5ml H₂O₂
 1:3 ratios: 10ml filtrate+30ml Acetone+5ml H₂O₂
 1:5 ratios: 10ml filtrate+50ml Acetone+ 5ml H₂O₂

Sl. No.	1:1 ratio			1:3 ratio			1:5 ratio		
	Name of the compound	Retention time (mins)	Relative Yield (%)	Name of the compound	Retention time (mins)	Relative Yield (%)	Name of the compound	Retention time (mins)	Relative Yield (%)
1.	Acetic acid	26.295	7.411	1H-Indol-5-ol	3.682	5.6	Oxirane,2-ethyl-2-methyl	3.270	7.747
2.	2-(2-buten-1-yl)-2-nitro	26.295	13.0710	Levoglucosene	4.666	5.66	Diethylene glycol hexylether	4.769	6.6515
3.	Ethyl ester	26.295	9.0419	Silacyclopent-3-ene-3-methyl	4.763	5.6	3(2H)-Isothiazolone,2-methyl	5.845	8.9991
4.	----	----	----	Butanedioic acid, Dimethyl ester	5.799	6.64	2(3H)-Oxazolethione,4-methyl	7.264	8.9991
5.	----	----	----	Hexanoic acid,4-oxo-methyl ester	7.247	6.64	2,4,6-Octatrienal	7.544	9.5312
6.	----	----	----	5-Nitro-m-Xylene	7.539	8.67	1,3-Pentadiene	10.863	5.2508
7.	----	----	----	2-Sec-Butylthiazole	9.530	6.53	Heptanoic acid	13.701	5.7124
8.	----	----	----	O-Methoxyacetophenone	9.885	7.80	4,4-dimethyl-cyclohex-2-en-1-ol	14.937	5.4777
9.	----	----	----	1,3-Pentadiene	10.331	3.87	Bicyclo[4.2.0] Octa-1,3,5-triene	15.212	8.1383
10.	----	----	----	Beta-D-Glucopyranose,1,6-anhydro-	13.289	3.46	N-Cyclo Oct 4-enyl acetamide	16.299	13.2248
11.	----	----	----	Beta-D-Glucopyranose,1,6-anhydro-	13.404	3.46	1H-Indene,2-Phenyl-	23.074	15.0246
12.	----	----	----	Butanedioic acid, Phenyl-	15.034	6.011		26.289	5.2429
13.	----	----	----	2-Methylbenzyl cyanide	15.166	6.011	----	----	----
14.	----	----	----	Beta-D-Glucopyranose,4-O-beta-D-galactopyranosyl	16.110	4.21	----	----	----
15.	----	----	----	Anthracene,9-methyl	23.051	11.1046	----	----	----
16.	----	----	----	Tetradecenoic acid	26.284	3.179	----	----	----
17.	----	----	----	3-Heptyne	27.817	5.5494	----	----	----

The absorption bands at 1045cm^{-1} , 1149cm^{-1} and 1407cm^{-1} attributed to C-O stretching vibrations confirms the presence of esters. The absorption bands in the range 1636cm^{-1} to 1680cm^{-1} indicates the presence of alkenes. The absorption bands at 1738cm^{-1} indicates the stretching vibrations of carbonyl, carboxylic acid and aldehyde groups. The absorption band at 2045cm^{-1} is attributed to alkyne, the absorption band at 2934cm^{-1} is attributed to stretching vibrations of C-H bond confirms the presence of alkane and also the vibrations in the range 1636cm^{-1} to $2,000\text{cm}^{-1}$ confirms the presence of conjugation. The absorption band at 3010cm^{-1} to 3100cm^{-1} confirms the presence of C-H stretchings in the aromatic rings and the detailed values are given in Table. 3. The FT-IR spectral studies of the aldol product for the molar ratios (1:1,1:3,1:5) indicates similar type of spectra's which attributes to the presence of functional groups such as hydroxyls, carbonyls, aldehydes, esters, carboxylic acids, alkanes, alkynes and also confirms the presence of aromatic rings with conjugation.

UV-Visible Spectral analysis

The Fig.6(b) shows UV-Visible spectra's for the aldol products for 1:1,1:3 and 1:5 ratios indicates the major peaks with maximum absorbance (λ_{max}) at 196nm and 197nm attributes for the presence of acids, esters, the absorbance at 194nm attributes for the presence of alkenes.

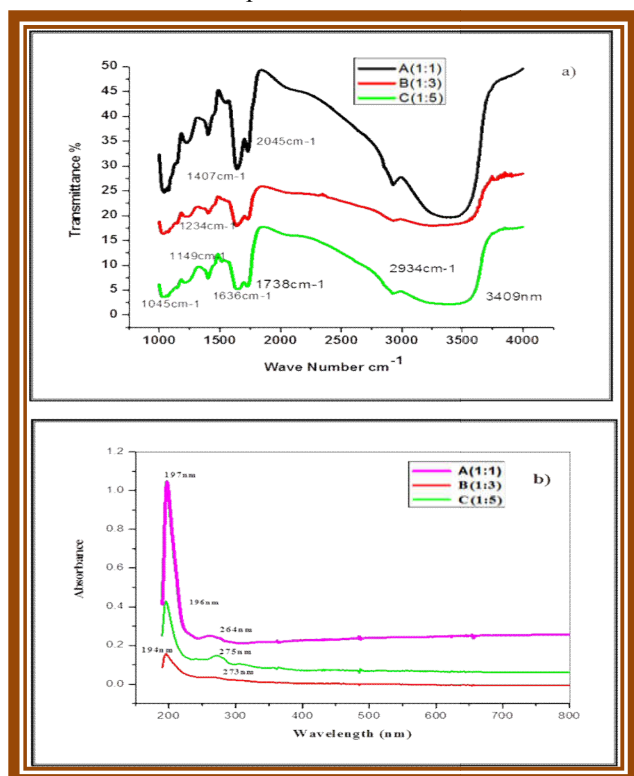


Figure 6 a) FT-IR absorption bands for the functional groups present in the aldol products for 1:1, 1:3, 1:5 ratios and **b)** UV-Visible absorption peak for the aldol products for 1:1,1:3 and 1:5 ratios.

The minor peak at 264nm shows the absorbance for acetone compound, absorbance at 273nm attributed for the presence of carboxylic acids, dienes and isoctane. Also absorbance peak at 275nm shows the presence of ketones/aldehydes, carbonyl groups and alcohols.

Table 3 FTIR absorption bands for functional groups present in the Aldol product for 1:1, 1:3, 1:5 ratios.

Sl. No.	Types of vibration	Wave number (cm^{-1})
1	OH broad band	3230-3550
2	C-H stretching band (Alkane)	2934
3	C=O	1738
4	C-O vibration	1045-1407
5	C-H stretching band (Aromatic rings) Conjugation	3010-3100
6	(Alkene and alkyne)	1636- 2000

Graphical abstract



CONCLUSION

In this present work, we demonstrated two steps insitu aldol condensation reaction as a synthetic strategy to convert the unused 30% DRB, a renewable biomass material into intermediate platform chemical and value added products in a simple, quick and economical method under microwave heating. Even though plenty of chemical building blocks already derived from various renewable bio resources, we made an attempt, to use DRB for the first time, as a renewable raw material which is an alternative low-cost feedstock which has eco-friendly properties like renewability, bio-compatibility and bio-degradability. Thus microwave assisted chemical process is proven to be one of the potential greener alternatives, chemical and energy intensive method under mild condition and/or lower manufacturing costs. These value added compounds have wide commercial and industrial applications.

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