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Reduce toxic emissions of As, Cr, and Cu phases during woody biomass gasification: A thermodynamic equilibrium study

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Abstract—Gasification of blended waste wood samples resulting from different activities and operations would be beneficial for reducing toxic emissions of metal(loid) elements while producing energy. This paper deals with willow wood (40%) and demolition waste wood (60%) gasification specifically focusing on the phase transformation temperature and speciation formation of As, Cr, and Cu which are regularly present in woody biomass. The gasification of mixed fuel was modelled under atmospheric pressure as typical reaction zones; partial combustion reaction (PCR) and boudouard reaction (BR). The PCR performed at temperature range of 0-1800 (°C) and both equivalence and steam/air ratios were 0.28 and 1:2, respectively. On the other hand, the BR model was operated from 0 to 1300 (°C) along with typical CO_2 to biomass ratio of 1:3. The samples were selected from ETI-UK database (83 willow wood) and ECN PHYLLIS2 database (9 demolition waste wood). Further, @Risk analysis simulation package was exploited to estimate the best composition data of each element in these samples. Refinement of the obtained results by PCR reveals that the phase transformation temperature of both As and Cr increased about 150 (°C) and 100 (°C), respectively, comparing to those obtained by gasification of willow wood. On the other hand, solid –gas phase transition of Cr was decreased about 100(°C) comparing to that when only demolition wood was gasified. In regards to BR, the phase transformation temperature of As, Cr, and Cu was similar (~1100(°C)) for all gasified woods. However, only concentration shifts were observed in gaseous phase of these elements. Eventually, the results from this study could be useful to reduce emissions and to disposal contamination waste wood via gasification process.

Keywords— Reduce toxic emissions; Waste wood; Elemental contaminants; Gasification; MTDATA.

I. INTRODUCTION

Presently, biomass as a form of alternative energy source contributes to 10%-14% of the global energy production, and it is estimated that this percentage will be increased up to 30%-40% in 2050 [1]. Furthermore, biofuels produced from biomass remarkably reduce the emissions of hazard gases such as $SO_x$and NO_x[2]. Examples of biomass as solid fuel resources include wood and its wastes, agricultural and herbaceous, municipal solid waste, human and animal wastes ,industrial waste, aquatic, and mixtures of these varieties [3],[4].

A significant proportion of the biomass energy is produced from woody biomass (wood and its wastes) which contributes about 64% of the total biomass energy [3]. Waste wood (WW) is known to be a solid recovered fuel and possesses a high degree of contaminations [5]. This is due to the fact that WW comprises a wide range of wood materials mostly resulted from demolition and construction operations, and from industrial and commercial activities [6], [7]. Consequently, WW is a very inhomogeneous fuel [4], hence, both its content and chemical compositions can be vastly diverse. For instance, wood treated with preservative compounds and surface materials contains elevated levels of metal(loid) elements such as As, Cr, Cu, Ni and Pb [8].

Biomass can be converted into different forms of energy via three principle types of conversion processes: thermochemical, biochemical and physical/chemical [9]. More recently, conversion of biomass to energy is carried out mainly by thermochemical and biochemical processes [10]. However, thermochemical conversions are widely used due to their higher yields and production rates of hydrogen as compared to biochemical techniques [11]. Typical thermochemical processes consist of exposing the biomass to high temperatures under oxygen conditions to yield solid, liquid and gas products, which can be upgraded to a range of usable fuels. Currently, the most popular advanced pathway among the thermochemical techniques is gasification.

Gasification offers a high flexibility regarding the utilization of the feedstock materials and genera on various forms of energy. Technically, gasification is an exothermic partial oxidation of biomass, operates at high temperature in the range of 800–1300(°C) with the presence of gasifying agents such as steam, air, oxygen, CO_2, or a combination of these agents[12], [13]. The product compositions and properties vary according to the biomass materials, gasifier type, and operational conditions.

The essence of gasification process is the conversion of solid carbonaceous fuels into combustible gases containing mainly a mixture of CO, CO_2, H_2, CH_4 , H_2O, N_2 and very small quantities of hydrocarbons and contaminants, like carbon particles, tar, and ash [14], [15].In general, biomass gasification consists of four main steps: biomass particles drying, pyrolysis of dried biomass particles (de-volatilization), partial oxidation of pyrolysis gases and/or char, and char gasification (reduction)) [12], and their relationships are depicted in Fig.1.[16]. In deed whatever the gasifier type is used, the principal chemical reactions in biomass gasification are provided (see Table I).

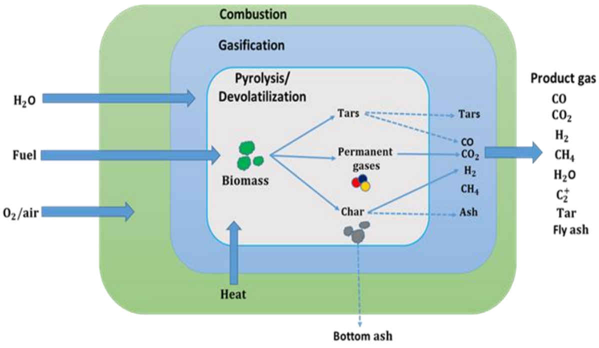


Fig. 1.Schematic of the processes in a gasifier.

TABLE.I. PRINCIPAL CHEMICAL REACTION IN BIOMASS GASIFICATION

Reaction	**Name**	**Number**
Biomass $\rightarrow$ char + tar + H_2O + light gases $(CO + CO_2 + H_2 + CH_4 + C_xH_yO_z + N_2 + \cdots)$	Pyrolysis and devolatilization	R1
Char combustion		
$C + \frac{1}{2}O_2 \rightarrow CO$ $C + O_2 \rightarrow CO_2$	Partial combustion Total combustion	R2 R3
Char gasification		
$C + CO_2 \rightleftarrows 2CO$ $C + H_2 \rightarrow CO + H_2$ $C + 2H_2 \leftrightarrows CH_4$	Boudouard reaction Steam gasification Hydrogene gasification	R4 R5 R6
Homogeneous reactions		
$CO + \frac{1}{2}O_2 \rightarrow CO_2$ $H_2 + \frac{1}{2}O_2 \rightarrow H_2O$ $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$ $CO + H_2O \leftrightarrows CO_2 + H_2$ $CO + 3H_2 \leftrightarrows CH_4 + H_2O$	CO oxidation H_2 oxidation CH_4 oxidation Water-gas shift (WGS) Methanation	R7 R8 R9 R10 R11
Tar conversion reactions		
$C_nH_m + (n/2)\,O_2 \rightarrow nCO + (m/2)H_2$ $C_nH_m + nH_2O \rightarrow (m/2 + n)H_2 + nCO_2$ $C_nH_m + nCO_2 \rightarrow 2nCO_2 + (m/2)H_2$ $C_nH_m \rightarrow (m/4)CH_4 + (n - m/4)C$	Partial oxidation Steam reforming Dry reforming Thermal cracking	R12 R13 R14 R15

Sours: [12];p.216

With thermal treatment of WW, metal(loid) elements will end up in bottom ash, or emit to the atmosphere[17]–[22]. However, high concentrations of these elements can cause severe environmental and technical problems as well as human health problems[5]. Therefore, the behaviour of metal(loid)s when conducting gasification requires further consideration, essentially, by characterizing the chemical compositions of the woody biomass and optimizing the operational parameters.

A range of studies[21]–[26] investigated the behavior of metal(loid) elements during the thermochemical process of biomass. It is found that the distribution of metal(loid) elements across the different ashes is dictated by several factors such as physical and chemical properties of the metal(loid)s, formed compounds during the thermal treatment, and operational conditions of the process.

A further few studies [27], [28] have indicated that the distribution of metal(loid) elements can be influenced, not only by the aforesaid factors, but also by the possible interactions between them during the thermal treatment. For instance, [28] reported that the interactions between As and the elements Hg, Cd and Sb alongside their relevant formed species may strongly affect the elements behavior. Thereupon, the possible interactions between metal(loid)s during the gasification must be further addressed.

In order to decrease the emissions of metal(loid) elements during gasification, and, hence mitigate their negative impacts, it is important to evaluate the distribution of these elements in gaseous and solid phases, and assess the formed species. Recent studies [17], [29] pointed out that, when considering multiple metal(loid) elements, thermodynamic equilibrium calculation can be a beneficial approach for specifying phase transformation of these elements and their relevant speciation formation.

Despite the fact that most of the solid-gaseous models provide useful information regarding the factors (e.g., operational conditions) that influence the partitioning of metal(loid)s, there is another factor as important as these factors: i.e., blending of different biomass samples which cannot be ignored, due to the different amounts of metal(loid)s present in waste and it may play a vital role in mitigating their emissions as a result of the occurred interactions and interferences between them.

The core objective of this paper is to explore the potential advantages of gasifying a mixture of woody biomass and in turn recommend a suitable configuration towards reducing the emissions of As, Cr, and Cu -elements. Willow wood and demolition wood were selected from the ETI-UK database [30] and ECN PHYLLIS2 database [31] respectively. Then, thermodynamic equilibrium modelling of gasification reactions, typical reaction zones; partial combustion reaction (PCR) and boudouard reaction (BR),were carried out using MTDATA thermodynamic software (Ver. 5.10 NPL, UK) to predict the phase transformation of the CCA-elements and to identify the generated chemical species under different operational conditions.

II. THERMODYNAMIC EQUILIBRIUM MODELLING

Thermodynamic equilibrium modelling of typical reaction zones; partial combustion reaction (PCR) and boudouard reaction (BR) (Table. I) in gasification were carried out using multiphase module of MTDATA software (Ver. 5.10 NPL, UK) to predict both solid-gaseous phase transformation and generate species of As, Cr and Cu in willow wood(W), demolition waste wood(Ww), and Mixing(60% Ww+40%W).

Willow wood (eighty three) samples and demolition wood (nine) samples with complete composition data were selected from the ETI-UK database [30] and ECN PHYLLIS2[31] database respectively as shown in Table II.

The best fit probability distribution for composition of willow wood samples including ultimate analysis (Table.III), proximate analysis (Table. IV, V and IV,), elements in dry sample (Table.VII, VIII, IX, and X), and elements in ash (Table. XI, XII, and XIII) were identified using @Risk analysis simulation package (Ver.6.1) add–in Microsoft Excel.

The composition to be introduced to the MTDATA include major elements (Ar, C, Ca, Cl, H, N, O, and S) and minor elements (As, Cr, Cu, Co, Fe, Na and Ni). Typical reaction zones; were selected in this paper partial combustion reaction (PCR) and boudouard reaction (BR) (Table. I) in gasification alongside with operation conditions as shown in Table .XIV. In this table, the process agents were based on types of reaction; partial combustion using Air with steam, while with boudouard reaction was used CO_2 The calculation of biomass feed depends on higher heating value (1) for willow woody biomass [32].

$$\mathrm{HHV_d} = (34.91\mathrm{C} + 117.83\mathrm{H} + 100.5\mathrm{S} - 1.5\mathrm{N} - 10.34\mathrm{O} - 2.11\mathrm{Ash}) \times 10^{-2} \qquad (1)$$

The mixing between willow wood (40 wt.%) and demolition wood (60 wt. %) consider systematically [24].

III. RESULTS AND DISCUSSION

The MTDATA-based models of typical reaction zones PCR and BR in gasification were operated sequentially at temperature range of 0-1800 (°C) and 0-1300 (°C), under standard atmosphere pressure (Table.XV) to predict the solid-gaseous phase transformation of the As, Cr, and Cu along with their speciation formation. The elemental data provided to MTDATA are given in Table. XVI and Table .XV corresponding to PCR and BR, respectively. Simulation results obtained from each reaction will individually be discussed in the following parts.

TABLE.II.SELECTED FUEL FROM FROM THE ETI-UK DATABASE AND ECN PHYLLIS2DATABASE,LISTED RESPECTIVELY

Sample	**FR Reference code**	**Sample**	**FR Reference code**
1	048/SRC-W/1/IF	***48***	046/SRC-W/17/IF
2	046/SRC-W/2/IF	***49***	047/SRC-W/17/IF
3	047/SRC-W/2/IF	***50***	048/SRC-W/17/IF
4	048/SRC-W/2/IF	***51***	046/SRC-W/18/IF
5	046/SRC-W/3/IF	***52***	047/SRC-W/18/IF
6	047/SRC-W/3/IF	***53***	048/SRC-W/18/IF
7	048/SRC-W/3/IF	***54***	046/SRC-W/19/IF
8	046/SRC-W/4/IF	***55***	047/SRC-W/19/IF
9	047/SRC-W/4/IF	***56***	048/SRC-W/19/IF
10	048/SRC-W/4/IF	***57***	046/SRC-W/20/IF
11	046/SRC-W/5/IF	***58***	047/SRC-W/20/IF
12	047/SRC-W/5/IF	***59***	048/SRC-W/20/IF
13	048/SRC-W/5/IF	***60***	103/Leaves
14	046/SRC-W/6/IF	***61***	104/Leaves
15	047/SRC-W/6/IF	***62***	105/Leaves
16	048/SRC-W/6/IF	***63***	106/Leaves
17	046/SRC-W/7/IF	***64***	107/Leaves
18	047/SRC-W/7/IF	***65***	108/Leaves
19	048/SRC-W/7/IF	***66***	109/Leaves
20	046/SRC-W/8/IF	***67***	110/Leaves
21	047/SRC-W/8/IF	***68***	111/Leaves
22	048/SRC-W/8/IF	***69***	048B/SRC-W/Nov15
23	046/SRC-W/9/IF	***70***	103B/SRC-W/Nov15
24	047/SRC-W/9/IF	***71***	113B/SRC-W/Nov15
25	048/SRC-W/9/IF	***72***	114B/SRC-W/Nov15
26	046/SRC-W/10/IF	***73***	017B/SRC-W/Nov15
27	047/SRC-W/10/IF	***74***	048B/SRC-W/Jan16
28	048/SRC-W/10/IF	***75***	103B/SRC-W/Jan16
29	046/SRC-W/11/IF	***76***	112B/SRC-W/Jan16
30	047/SRC-W/11/IF	***77***	113B/SRC-W/Jan16
31	048/SRC-W/11/IF	***78***	114B/SRC-W/Jan16
32	046/SRC-W/12/IF	***79***	017B/SRC-W/Jan16
33	047/SRC-W/12/IF	***80***	048B/SRC-W/Mar16
34	048/SRC-W/12/IF	***81***	112B/SRC-W/Mar16
35	046/SRC-W/13/IF	***82***	113B/SRC-W/Mar16
36	047/SRC-W/13/IF	***83***	114B/SRC-W/Mar16
37	048/SRC-W/13/IF	***84***	#871
38	046/SRC-W/14/IF	***85***	#679
39	047/SRC-W/14/IF	***86***	#2900
40	048/SRC-W/14/IF	***87***	#2901
41	046/SRC-W/15/IF	***88***	#3498
42	047/SRC-W/15/IF	***89***	#1364
43	048/SRC-W/15/IF	***90***	#1448
45	046/SRC-W/16/IF	***91***	#1779
46	047/SRC-W/16/IF	***92***	#2712
47	048/SRC-W/16/IF		

Notes: the references code (1-83) Sours: [30]and the references code (84-92) Sours:[31].

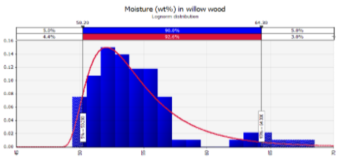
A. *Phase Transformation and Released Species of As, Cr, and Cu element in willow wood under PCR and BR*

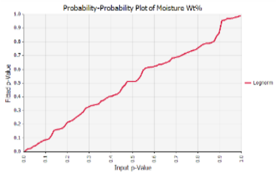
1) *Under PCR*

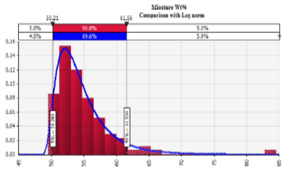
a) *Arsenic*

The solid-gaseous transformation of As starts at 1250 (°C), and completely transformed to gaseous at temperature ≥ 1400 (°C) (Fig 2a). In term of speciation formation, As distributed in solid phase as dominant species $AsNa_3$ and As_2Ni_5, meanwhile the revealed species in gaseous phase are As, As_2, As_3, AsH, AsH_2, AsH_3 and AsN as illustrated in Fig 2b.

TABLE.III.STATISTICAL ANALYSIS OF ULTIMATE ANALYSIS (%)

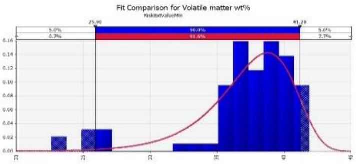


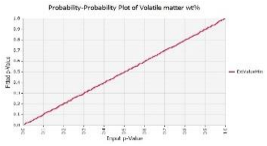


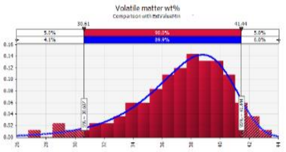


Probability Distribution -Log norm

Moisture content	***Data***	***Min***	***Max***	***Mean***	***Std.Dev***
	Input	***49.40***	***68.50***	***54.59***	***4.00***
	P.D	***48.17***	***+ ∞***	***54.59***	***4.04***

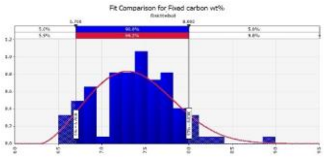


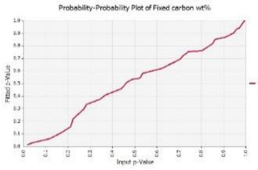


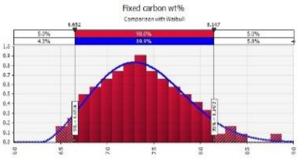


Probability Distribution- Ext value Min

Volatile matter content	***Data***	***Min***	***Max***	***Mean***	***Std.Dev***
	Input	22.6	41.9	37.1	4.34
	P.D	-∞	+ ∞	37.3	3.3

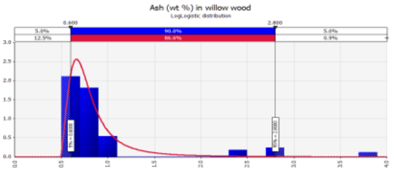


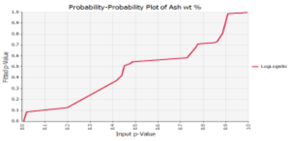


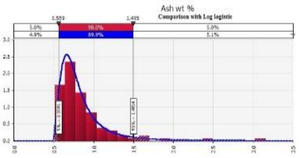


Probability Distribution- *Weibull*

Fixed carbon Content	Data	***Min***	***Max***	***Mean***	***Std.Dev***
	Input	6.5	9.0	7.3	0.46
	P.D	6.3	+ ∞	7.4	0.46



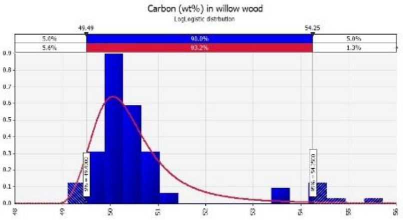


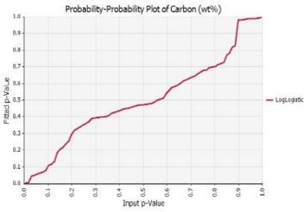


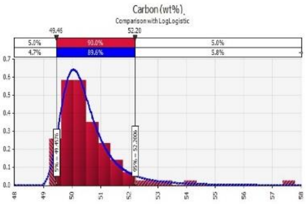
Probability Distribution- *Log logistic*

Ash Content	***Data***	***Min***	***Max***	***Mean***	***Std.Dev***
	Input	0.5	3.9	0.8	0.7
	P.D	0.49	+	0.86	0.77

TABLE.IV.STATISTICAL ANALYSIS OF PROXIMATE ANALYSIS (%)







Probability Distribution- *Log Logistic*

Carbon (C)	***Data***	***Min***	***Max***	***Mean***	***Std.Dev***
	Input	49.1	55.7	50.65	1.3523
	P.D	48.90	+∞	50.54	1.16

TABLE.V.STATISTICAL ANALYSIS OF PROXIMATE ANALYSIS (%)

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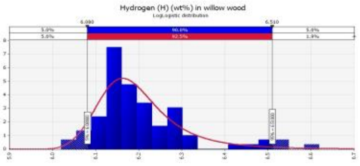
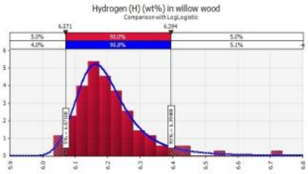
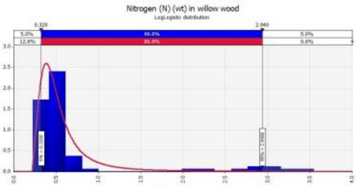
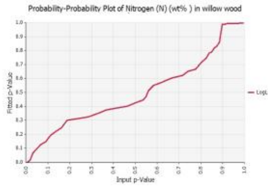
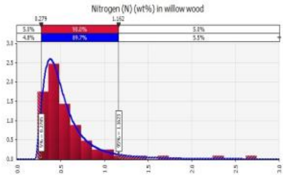
<tr><td colspan="2"> </td><td colspan="2"> </td><td colspan="2"> </td></tr>
<tr><td colspan="6">Probability Distribution- <i>Log Logistic</i></td></tr>
<tr><td rowspan="3"><i>Hydrogen
(H)</i></td><td><i>Data</i></td><td><i>Min</i></td><td><i>Max</i></td><td><i>Mean</i></td><td><i>Std.Dev</i></td></tr>
<tr><td><i>Input</i></td><td>6.02</td><td>6.62</td><td>6.2</td><td>1.11</td></tr>
<tr><td><i>P.D</i></td><td>5.96</td><td>+∞</td><td>6.2</td><td>0.11</td></tr>
<tr><td colspan="2"> </td><td colspan="2"> </td><td colspan="2"> </td></tr>
<tr><td colspan="6">Probability Distribution- <i>Log Logistic</i></td></tr>
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(N)</i></td><td><i>Data</i></td><td><i>Min</i></td><td><i>Max</i></td><td><i>Mean</i></td><td><i>Std.Dev</i></td></tr>
<tr><td><i>Input</i></td><td>0.22</td><td>3.55</td><td>0.72</td><td>0.77</td></tr>
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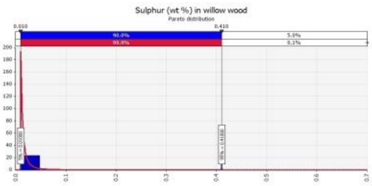
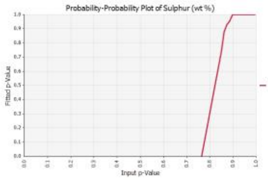
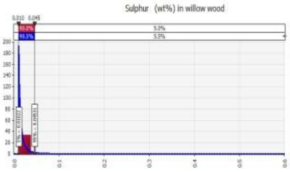
<tr><td colspan="2"> </td><td colspan="2"> </td><td colspan="2"> </td></tr>
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(S)</i></td><td><i>Data</i></td><td><i>Min</i></td><td><i>Max</i></td><td><i>Mean</i></td><td><i>Std.Dev</i></td></tr>
<tr><td><i>Input</i></td><td>0.01</td><td>0.66</td><td>0.059</td><td>0.140</td></tr>
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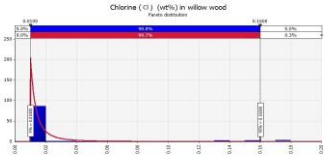
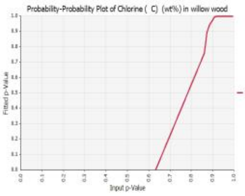
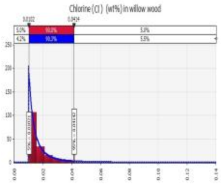
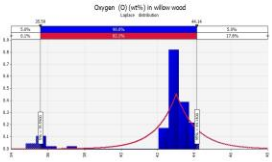
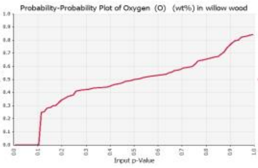
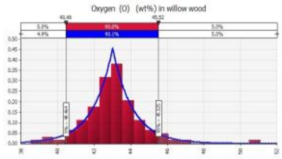
<tr><td colspan="2"> </td><td colspan="2"> </td><td colspan="2"> </td></tr>
<tr><td colspan="6">Probability Distribution -<i>Log norm</i></td></tr>
<tr><td rowspan="3"><i>Chlorine
(Cl)</i></td><td><i>Data</i></td><td><i>Min</i></td><td><i>Max</i></td><td><i>Mean</i></td><td><i>Std.Dev</i></td></tr>
<tr><td><i>Input</i></td><td>0.01</td><td>0.12</td><td>0.018</td><td>0.015</td></tr>
<tr><td><i>P.D</i></td><td>0.01</td><td>+∞</td><td>0.0196</td><td>0.068</td></tr>
<tr><td colspan="2"> </td><td colspan="2"> </td><td colspan="2"> </td></tr>
<tr><td colspan="6">Probability Distribution- <i>Ext value Min</i></td></tr>
<tr><td rowspan="3"><i>Oxygen
(O)</i></td><td><i>Data</i></td><td><i>Min</i></td><td><i>Max</i></td><td><i>Mean</i></td><td><i>Std.Dev</i></td></tr>
<tr><td><i>Input</i></td><td>34.79</td><td>44.28</td><td>42.33</td><td>2.35</td></tr>
<tr><td><i>P.D</i></td><td>-∞</td><td>+∞</td><td>43.0</td><td>1.55</td></tr>
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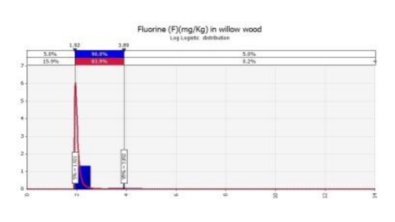
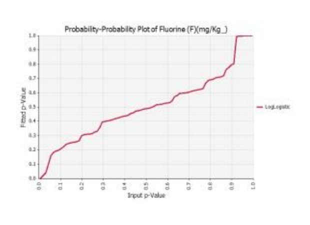
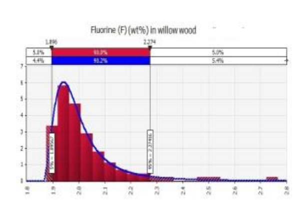
TABLE.VI.STATISTICAL ANALYSIS OF PROXIMATE ANALYSIS (%)



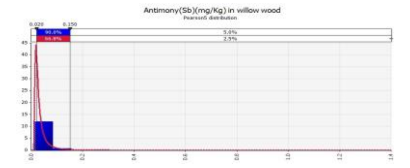


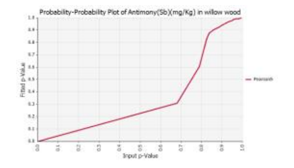


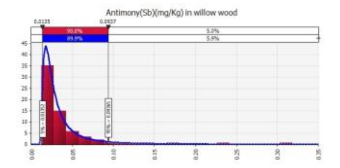
Probability Distribution- *Weibull*

	Data	Min	Max	Mean	Std.Dev
Fluorine (F)	***Input***	1.870	13.64	2.25	1.36
	P.D	1.86	+∞	2.02	0.28

TABLE.VII. STATISTICAL ANALYSIS OF ELEMENTS IN DRY SAMPLE(mg/kg)

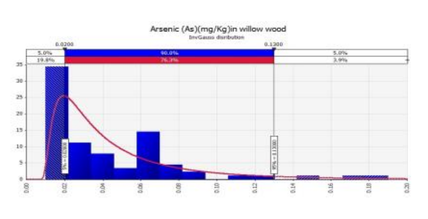


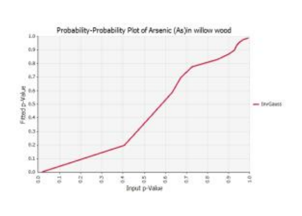


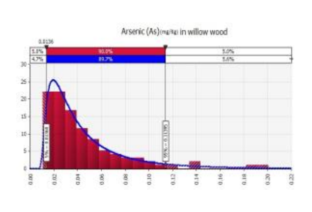


Probability Distribution- *Pareto*

	Data	Min	Max	Mean	Std.Dev
(Antimony (Sb)	***Input***	0.01	1.27	0.055	0.144
	P.D	0.008	+∞	0.041	N/A

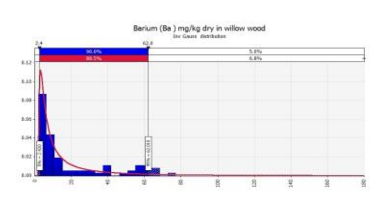


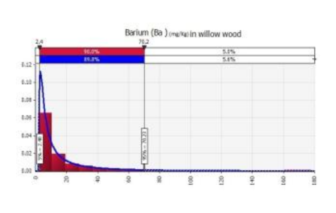




Probability Distribution- *Inv Gauss*

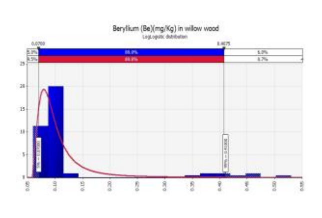
	Data	Min	Max	Mean	Std.Dev
Arsenic (As)	***Input***	0.01	0.19	0.046	0.036
	P.D	0.006	+∞	0.046	0.037

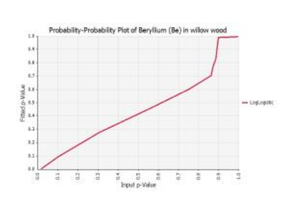


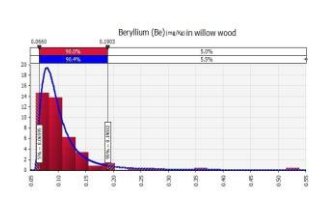


Probability Distribution- *Inv Gauss*

	Data	Min	Max	Mean	Std.Dev
Barium (Ba)	***Input***	1.85	77.26	19.75	21.72
	P.D	1.19	+∞	19.75	34.32



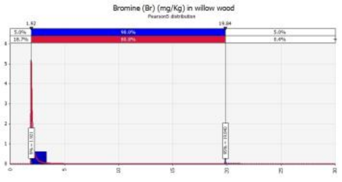


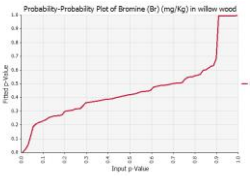


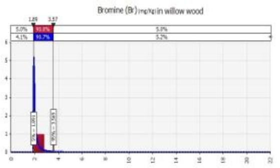
Probability Distribution-*Log Logistic*

	Data	Min	Max	Mean	Std.Dev
Beryllium (Be)	***Input***	0.06	0.53	0.126	0.01
	P.D	0.058	+∞	0.109	0.129

TABLE.VIII. STATISTICAL ANALYSIS OF ELEMENTS IN DRY SAMPLE(mg/kg)

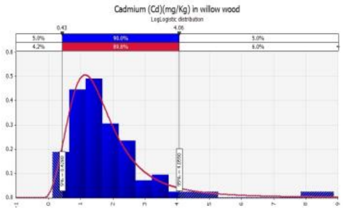


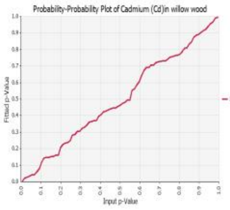


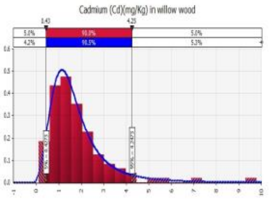


Probability Distribution-*Pearson*

	Data	Min	Max	Mean	Std.Dev
Bromine (Br)	Input	1.87	27.25	3.78	5.6
	P.D	1.86	+∞	3.64	N/A

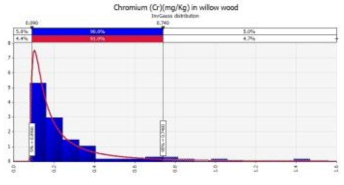


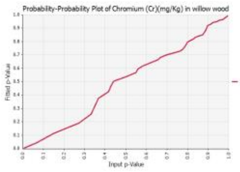


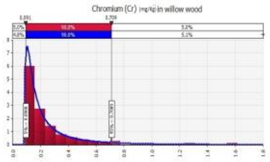


Probability Distribution-*Log Logistic*

	Data	Min	Max	Mean	Std.Dev
Cadmium (Cd)	Input	0.13	8.88	1.84	1.43
	P.D	-0.12	+∞	1.86	1.73

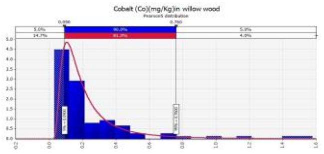


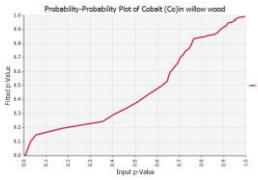


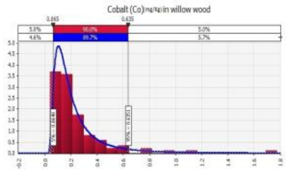


Probability Distribution-*Inv Gauss*

	Data	Min	Max	Mean	Std.Dev
Chromium (Cr	Input	0.08	1.47	0.256	0.23
	P.D	0.0697	+∞	0.256	0.25

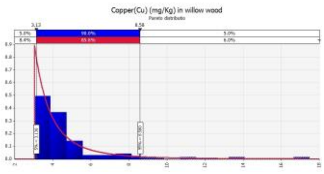


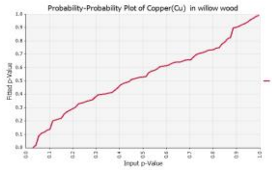


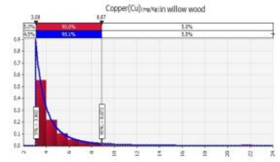


Probability Distribution-*Pearson5*

	Data	Min	Max	Mean	Std.Dev
Cobalt (Co)	Input	0.03	1.58	0.259	0.28
	P.D	0.00073	+∞	0.255	0.414



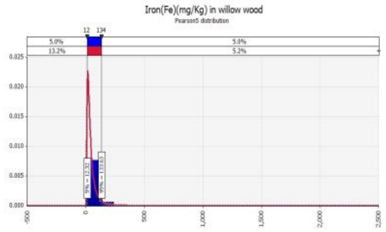
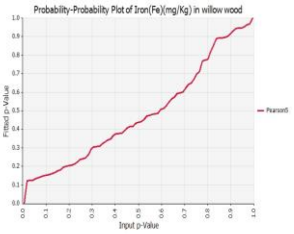
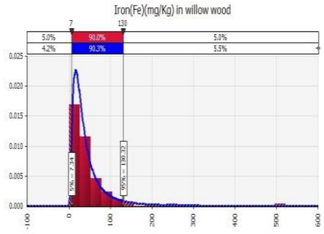
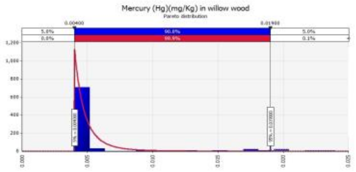
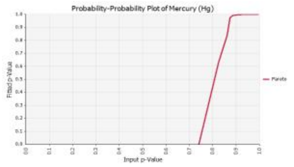
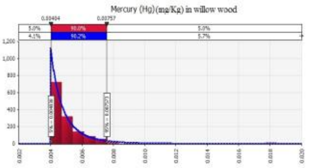
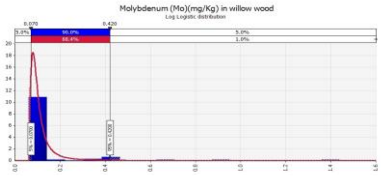
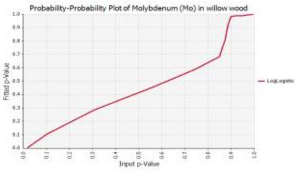
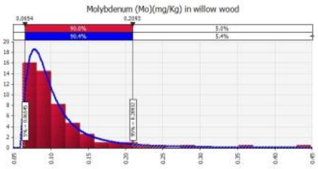




Probability Distribution- *Pareto*

	Data	Min	Max	Mean	Std.Dev
Copper (Cu)	Input	3.0	17.5	4.7	2.3
	P.D	3.0	+	4.8	3.46

TABLE.IX. STATISTICAL ANALYSIS OF ELEMENTS IN DRY SAMPLE(mg/kg)

<table>
<tr><td colspan="2"> </td><td colspan="2"> </td><td colspan="2"> </td></tr>
<tr><td colspan="6">Probability Distribution-<i>Pearson5</i></td></tr>
<tr><td rowspan="3"><i>Iron
(Fe)</i></td><td><i>Data</i></td><td><i>Min</i></td><td><i>Max</i></td><td><i>Mean</i></td><td><i>Std.Dev</i></td></tr>
<tr><td><i>Input</i></td><td>0.13</td><td>8.88</td><td>1.84</td><td>1.43</td></tr>
<tr><td>P.D</td><td>-0.12</td><td>+∞</td><td>1.86</td><td>1.73</td></tr>
<tr><td colspan="2"> </td><td colspan="2"> </td><td colspan="2"> </td></tr>
<tr><td colspan="6">Probability Distribution-<i>Pareto</i></td></tr>
<tr><td rowspan="3"><i>Mercury
(Hg)</i></td><td><i>Data</i></td><td><i>Min</i></td><td><i>Max</i></td><td><i>Mean</i></td><td><i>Std.Dev</i></td></tr>
<tr><td><i>Input</i></td><td>0.004</td><td>0.024</td><td>0.059</td><td>0.0047</td></tr>
<tr><td>P.D</td><td>0.004</td><td>+∞</td><td>0.051</td><td>0.0015</td></tr>
<tr><td colspan="2"> </td><td colspan="2"> </td><td colspan="2"> </td></tr>
<tr><td colspan="6">Probability Distribution- <i>LogLogistic</i></td></tr>
<tr><td rowspan="3"><i>Molybdenum
(Mo)</i></td><td><i>Data</i></td><td><i>Min</i></td><td><i>Max</i></td><td><i>Mean</i></td><td><i>Std.Dev</i></td></tr>
<tr><td><i>Input</i></td><td>0.06</td><td>1.44</td><td>0.146</td><td>0.196</td></tr>
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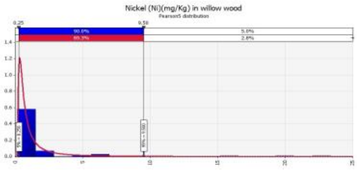
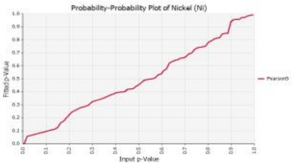
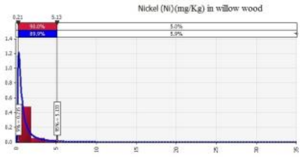
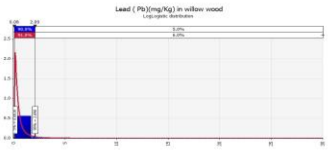
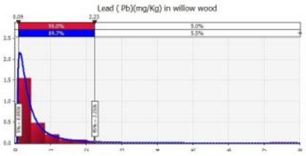
<tr><td colspan="2"> </td><td colspan="2"> </td><td colspan="2"> </td></tr>
<tr><td colspan="6">Probability Distribution- <i>Pearson5</i></td></tr>
<tr><td rowspan="3"><i>Nickel
(Ni)</i></td><td><i>Data</i></td><td><i>Min</i></td><td><i>Max</i></td><td><i>Mean</i></td><td><i>Std.Dev</i></td></tr>
<tr><td><i>Input</i></td><td>0.13</td><td>23.4</td><td>1.92</td><td>3.96</td></tr>
<tr><td><i>P.D</i></td><td>0.053</td><td>+</td><td>2.64</td><td>N/A</td></tr>
<tr><td colspan="2"> </td><td colspan="2"> </td><td colspan="2"> </td></tr>
<tr><td colspan="6">Probability Distribution-<i>Log Logistic</i></td></tr>
<tr><td rowspan="3"><i>Lead
(Pb)</i></td><td><i>Data</i></td><td><i>Min</i></td><td><i>Max</i></td><td><i>Mean</i></td><td><i>Std.Dev</i></td></tr>
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<tr><td><i>P.D</i></td><td>0.059</td><td>+</td><td>0.88</td><td>N/A</td></tr>
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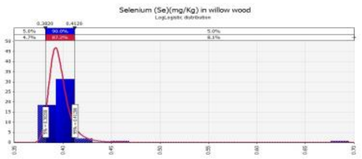
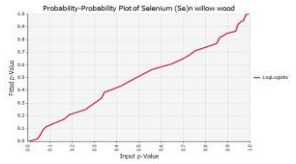
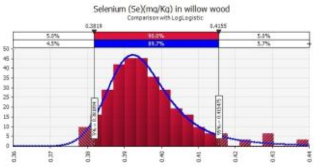
TABLE.X.STATISTICAL ANALYSIS OF ELEMENTS IN DRY SAMPLE(mg/Kg)

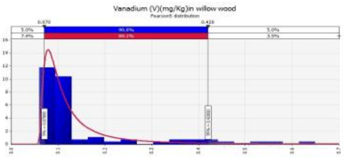


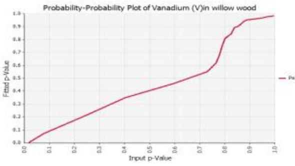


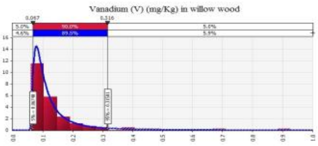


Probability Distribution-*Log Logistic*

Selenium (Se)	***Data***	***Min***	***Max***	***Mean***	***Std.Dev***
	Input	0.374	0.695	0.399	0.0345
	P.D	0.367	+∞	0.369	0.0118

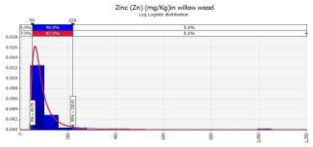


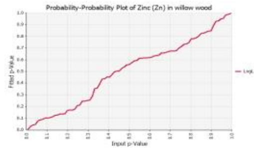


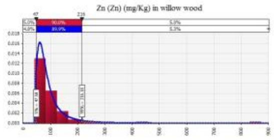


Probability Distribution- *LogLogistic*

Vanadium (V)	***Data***	***Min***	***Max***	***Mean***	***Std.Dev***
	Input	0.06	0.65	0.148	0.125
	P.D	0.0499	+∞	0.1525	N/A



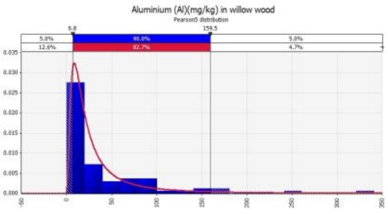


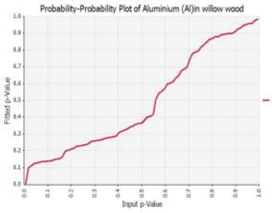


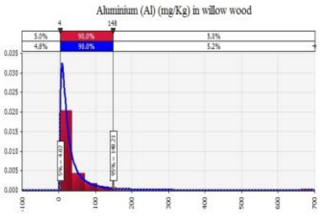
Probability Distribution- *Pearson*

Zinc (Zn)	***Data***	***Min***	***Max***	***Mean***	***Std.Dev***
	Input	40.83	1,054.96	106.20	121.12
	P.D	39.15	+∞	103.57	N/A

TABLE.XI.STATISTICAL ANALYSIS OF ELEMENTS IN ASH (mg/Kg)

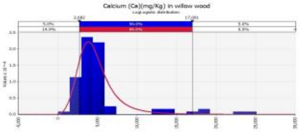


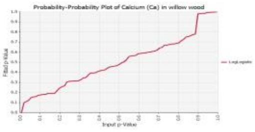


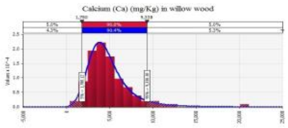


Probability Distribution-*Pearson5*

Aluminum (Al)	***Data***	***Min***	***Max***	***Mean***	***Std.Dev***
	Input	0.00	341.53	42.29	57.27
	P.D	3.19	+∞	51.44	N/A



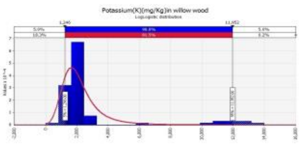


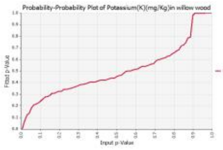


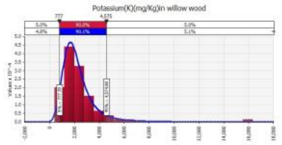
Probability Distribution-*Log Logistic*

Calcium (Ca)	***Data***	***Min***	***Max***	***Mean***	***Std.Dev***
	Input	0.00	25,136.0	5,513.48	4,407.8
	P.D	530.1	+∞	4,885.44	2,726.9

TABLE XII.STATISTICAL ANALYSIS OF ELEMENTS IN ASH (mg/Kg)

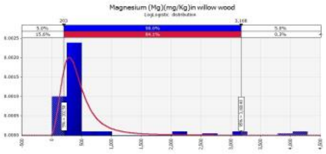


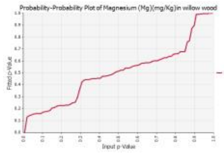


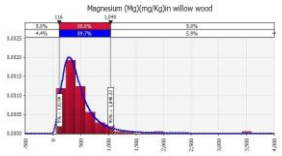


Probability Distribution- *LogLogistic*

	Data	Min	Max	Mean	Std.Dev
Potassium (K)	***Input***	0.00	14,012.0	2,870.73	3,111.0
	P.D	147.5	+∞	2,247.53	1,435.5

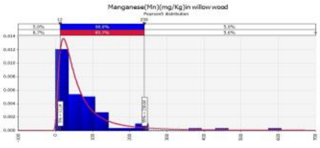


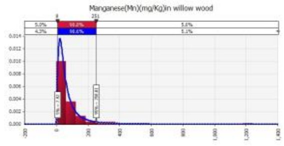




Probability Distribution- *LogLogistic*

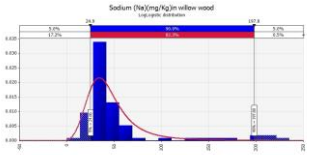
	Data	Min	Max	Mean	Std.Dev
Magnesium (Mg)	***Input***	0.00	4,289.34	639.46	887.73
	P.D	20.91	+∞	476.56	440.90

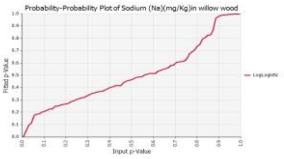


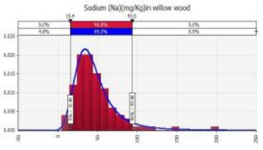


Probability Distribution-*Log Logistic*

	Data	Min	Max	Mean	Std.Dev
Manganese (Mn)	***Input***	0.00	609.55	78.07	97.11
	P.D	12.51	+∞	83.57	346.03

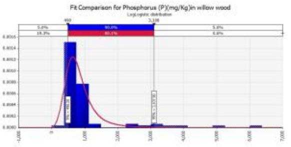


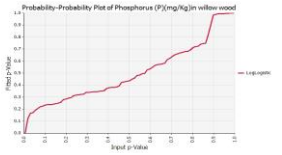


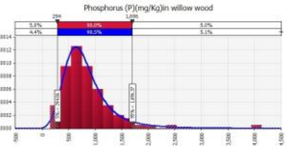


Probability Distribution-*Log Logistic*

	Data	Min	Max	Mean	Std.Dev
Sodium (Na)	***Input***	0.00	235.47	54.93	48.84
	P.D	3.57	+∞	47.23	31.63







Probability Distribution- *Pearson*

	Data	Min	Max	Mean	Std.Dev
Phosphorus (P)	***Input***	0.00	6,386.2	1,028.1	1,028.05
	P.D	65.79	+∞	848.50	516.76

TABLE XIII.STATISTICAL ANALYSIS OF ELEMENTS IN ASH (mg/Kg)

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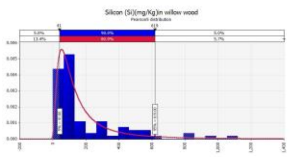
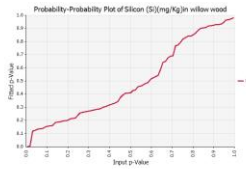
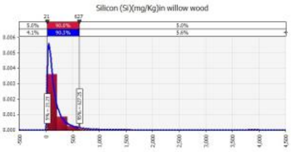
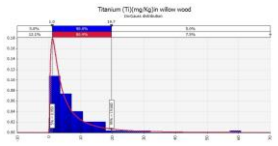
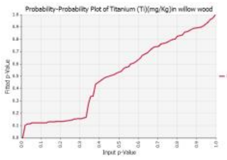
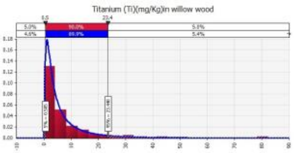
<tr><td colspan="2"> </td><td colspan="2"> </td><td colspan="2"> </td></tr>
<tr><td colspan="6">Probability Distribution- <i>Log Logistic</i></td></tr>
<tr><td rowspan="3"><i>Silicon
(Si)</i></td><td><i>Data</i></td><td><i>Min</i></td><td><i>Max</i></td><td><i>Mean</i></td><td><i>Std.Dev</i></td></tr>
<tr><td><i>Input</i></td><td>0.00</td><td>1,122.00</td><td>201.73</td><td>22913</td></tr>
<tr><td><i>P.D</i></td><td>25.80</td><td>+∞</td><td>220.26</td><td>N/A</td></tr>
<tr><td colspan="2"> </td><td colspan="2"> </td><td colspan="2"> </td></tr>
<tr><td colspan="6">Probability Distribution- <i>Pearson</i></td></tr>
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(Ti)</i></td><td><i>Data</i></td><td><i>Min</i></td><td><i>Max</i></td><td><i>Mean</i></td><td><i>Std.Dev</i></td></tr>
<tr><td><i>Input</i></td><td>0.00</td><td>60.840</td><td>6.963</td><td>8.735</td></tr>
<tr><td><i>P.D</i></td><td>0.394</td><td>+∞</td><td>6.963</td><td>9.453</td></tr>
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TABLE.XIV. SIMULATION PARAMETERS FOR GASIFICATION- (PCR AND BR)-MODELS

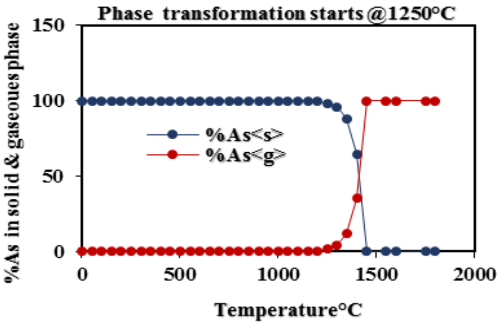
Parameters	***Range/Value GPCR***	***Range/Value GBR***
Temperature range (°C)	0-1800	0-1300
Pressure (atm)	1	1
Equivalence ratio	0.28	0
Biomass rate (Kg/h)	1.23	1.23
Air rate (m^3/h)	0.34	0.0
Steam rate (m^3/h)	0.68	0.0
Steam /Air	2:1	0.0
CO_2(m^3/h)	0.0	0.41
CO_2/Biomass	0.0	1:3

TABLE.XVI. ELEMENTAL MASS PROVIDED TO MDTATA PCR IN GASIFICATION (WILLOW WOOD, DEMOLITION WASTE WOOD, AND MIXING DEMOLITION WASTE WOOD 60% AND WILLOW WOOD 40%).

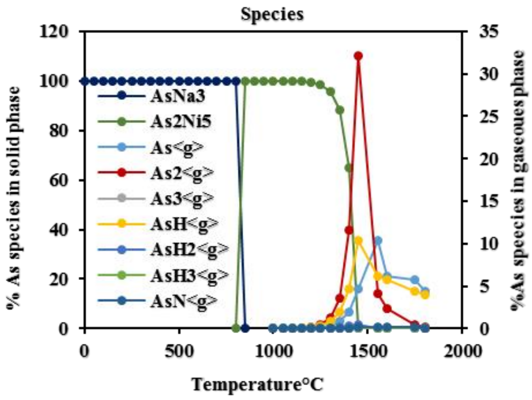
Element	**Test 1 (GPCR)**	**Test 2 (GPCR)**	**Test 3 (GPCR)**
	Willow Wood	***Demolition Waste Wood (WW)***	***Mix 60WW+40Willow***
Ar	0.248	0.248	0.248
N	40.26196	41.65	41.00986
O	228.8363	142.01	176.0572
C	149.645	139.39	142.7304
H	694.976	743.1	721.5533
S	0.02136	0.09	0.063466
Cl	0.02136	563.2	334.843
Cu	2.67	6.85	5.141779
Cr	0.17088	20.71	12.3856
Co	0.150944	1.03	0.676614
Ni	1.3884	6.57	4.464454
As	0.020292	1.34	0.80933
Na	85.12672	796	507.289
Ca	42443.39	2617.15	18533.3
Fe	2985.665	314.48	1381.236

TABLE XV. ELEMENTAL MASS PROVIDED TO MDTATA BR IN GASIFICATION (WILLOW WOOD, DEMOLITION WASTE WOOD, AND MIXING DEMOLITION WASTE WOOD 60% AND WILLOW WOOD 40%).

Element	**Test 1 (GBR)**	**Test 2 (GBR)**	**Test 3 (GBR)**
	Willow Wood	***Demolition Waste Wood (WW)***	***Mix 60WW+40Willow***
Ar	0.00	0.00	0.00
N	2.72	1.44892	1.947519
O	116.70	203.6028	168.4168
C	139.50	149.74748	145.1377
H	261.71	215.024	232.7422
S	0.09	0.02136	0.049431
Cl	563.2	0.02136	223.2358
Cu	6.85	2.67	4.317853
Cr	20.71	0.17088	8.314024
Co	1.03	0.150944	0.50139
Ni	6.57	1.3884	3.439102
As	1.34	0.020292	0.546318
Na	796	85.12672	366.5682
Ca	2617.15	42443.388	26503.33
Fe	314.48	2985.6652	1916.046



a) % As phase transition



b)

% As species

Fig. 2. Arsenic phase transformation and equilibrium composition under PCR gasification (willow wood).

b) *Chromium*

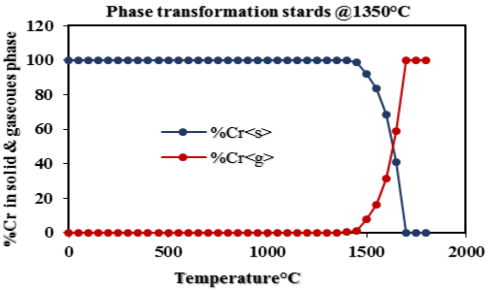
Fig. 3a shows the solid–gaseous phase transition of Cr. It can be seen that, when the temperate is less than 1350 (°C), Cr remained in solid phase as dominant specie C_3Cr_7 (Fig. 3b). Above 1350 (°C), Cr transferred into gaseous phase as ClCr, Cl_2Cr, Cr, Cr_2CrH, CrHO, CrN, CrO, and CrS as shown in Fig 3b

c) *Copper*

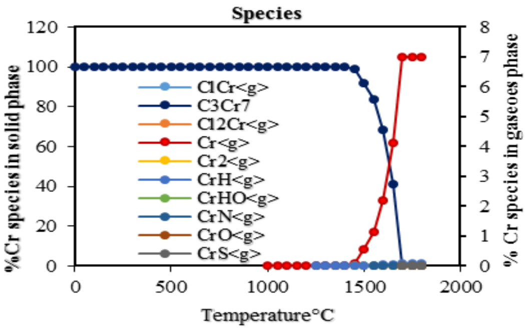
Copper remained totally in solid phase (Fig 4b) as dominant specie CaCu when the temperature less than 1350 (°C). Whereas, at temperature above 1350 (°C), Cu completely released into the gaseous species CuH, Cu, Cu_2, and CuCl as shown in Fig 4a and b

2) *Under BR*

In this case, the elements As, Cr, and Cu remained in solid phase at temperature lower than 1100 (°C) as depicted in the Fig.5. Table.XVII. summarized the speciation formation during solid phase and gaseous phases. It is obvious that, As primarily occurs in the form of $AsNa_3$ in solid phase when the temperature is ~≤ 800 (°C), then it transformed into dominant specie As_2Ni_5 at temperature between 800 (°C) and 1300 (°C). Further, Cu and Cr remained in solid phase as CaCu and C_3Cr_7, respectively, at temperature between 0-1300 (°C).

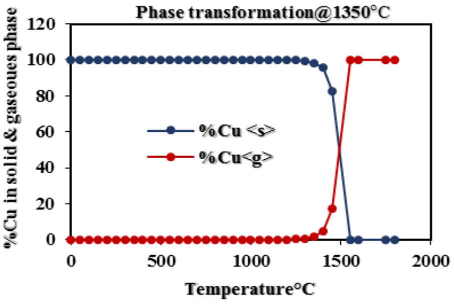


a) %Cr phase transition

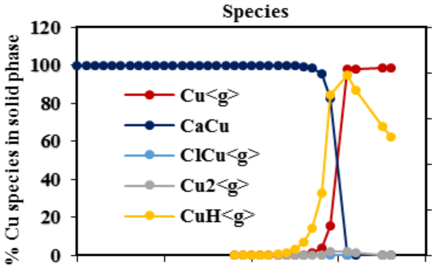


b) %Cr species

Fig. 3. Chromium phase transformation and equilibrium composition under PCR gasification (willow wood).

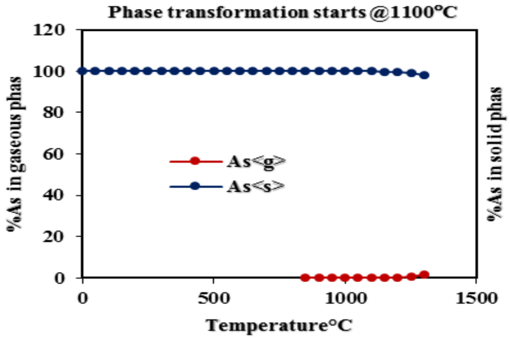


a) % Cu phase transition

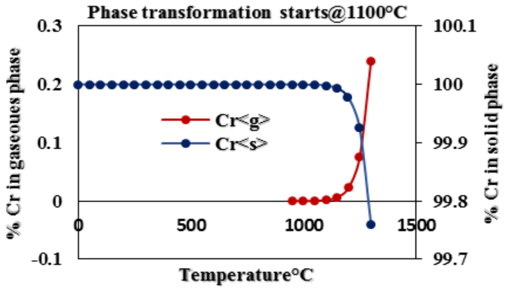


b) % Cu species

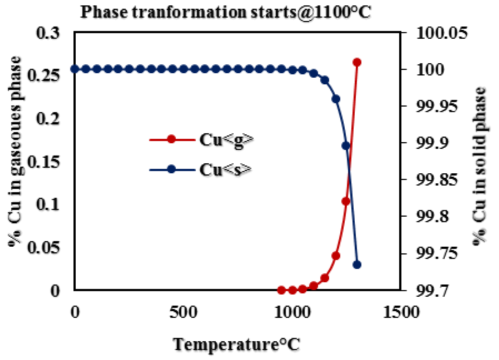
Fig. 4. Copper phase transformation and equilibrium composition under PCR gasification (willow wood).



a) % As phase transition



b) % Cr phase transition



C) % Cu phase transition

Fig. 5. As, Cr, and Cu –elements phase transformation temperature under BR gasification (willow wood).

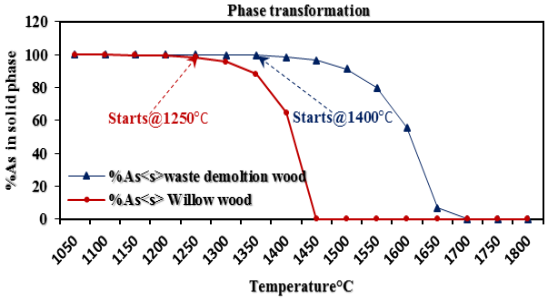
TABLE.XVII.THE MAIN SPECIES FORMED IN REACTION BR IN GASIFICATION SYSTEM

Elements	Dominant species in solid phase& gaseous phase			
	T. **℃**	***Solid phase***	***T.*** **℃**	***Gaseous phase***
As	0-800	$AsNa_3$	1100-1300	As, As_2, AsH, AsH_2
	850-1300	As_2Ni_5	1100-1300	AsH_3
Cr	0-1300	C_3Cr_7	1000-1300	Cr
			1250-1300	CrCl
			1300	CrH
Cu	0-1300	CaCu	900-1300	Cu,CuH
			1100-1300	Cu_2,ClCu

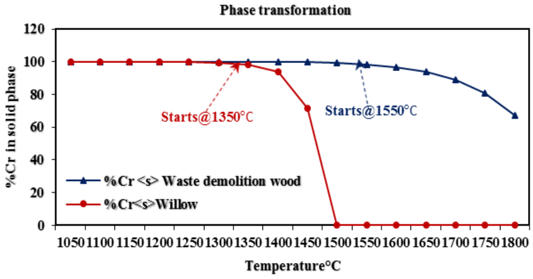
B. *Transformation and Released Species of As, Cr, and Cu element in demolition woodunder PCR and BR*

1) *Under PCR*

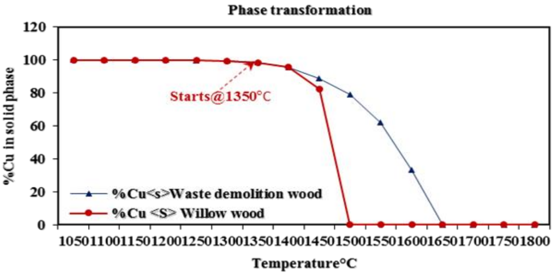
With regard to demolition wood, it is observed that As and Cr totally remained in solid phase at temperature ≤ 1400(°C) and ≤ 1550 (°C) respectively. As such, the phase transformation temperature of As and Cr increased, sequentially, ~150(°C) and ~200(°C) compared to their transformation temperatures when willow wood is gasified (Fig.6.a and b). However, Cu exhibited same behavior during the gasification of each wood type, that is, it completely remained in solid phase at temperature ~≤1350 (°C), as shown in Fig.6.c. On the other hand, the formed species in condensed and gaseous phases are similar under PCR during the gasification of each type of wood.



a) % As phase transition



b) % Cr phase transition

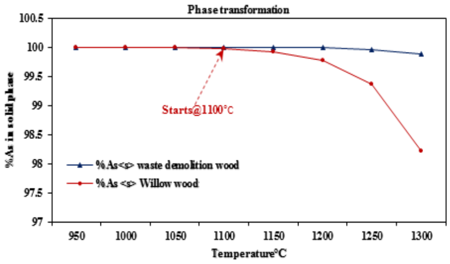


c) % Cu phase transition

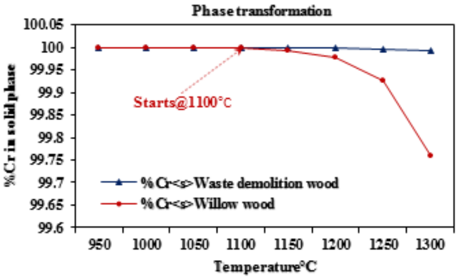
Fig. 6.Comparison between the transformation behaviour of As, Cr, and Cu in demolition wood, and feed stock -willow wood under PCR gasification atmosphere (1atm) at temperature between 0-1800 °C.

2) *Under BR*

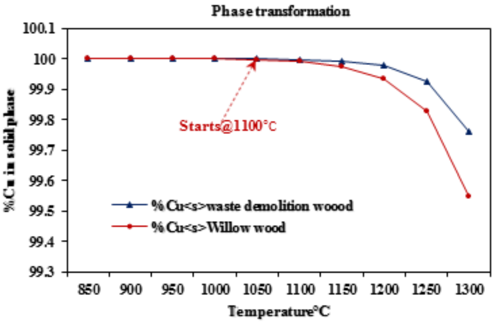
Fig.7. (a, b, and c) demonstrates the results of As, Cr, and Cu during BR. It is clear that these elements remained (about 100%) in solid phase at temperature range 0-1300 (°C). On the other hand, similar solid and gaseous species are formed during the gasification of each wood type



a) % As phase transition



b) %Cr phase transition



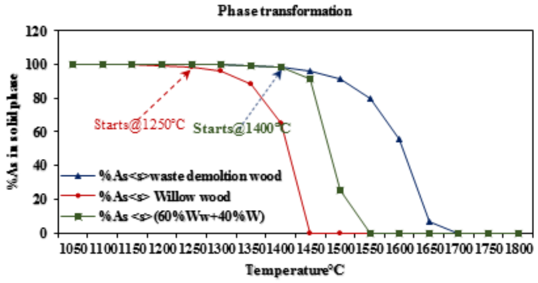
c) % Cu phase transition

Fig. 7.Comparison between the transformation behaviour of As, Cr, and Cu in demolition wood, and feed stock -willow wood under BR gasification atmosphere (1atm) at temperature between 0-1300 °C.

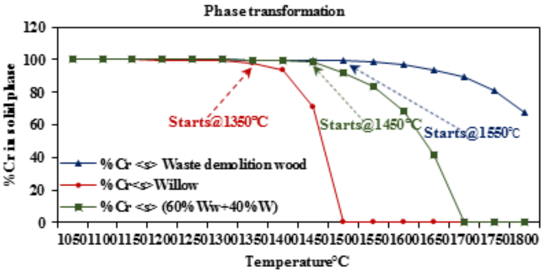
C. *Effect of mixing demolition and willow woods on the behaviors of element (As, Cr,and Cu) under PCR and BR*

Each gasified sample comprises demolition wood (60%) and willow wood (40%). The simulation results of PCR model indicate that the threshold temperatures of As and Cr are improved by 150 (°C) and 100 (°C), respectively, compared to their threshold temperatures when only willow wood is considered, as demonstrated in Fig.8. a and b; whereas Cu shows same behaviour during the gasification of the blended woods and of the willow wood, as shown in Fig.8.c,

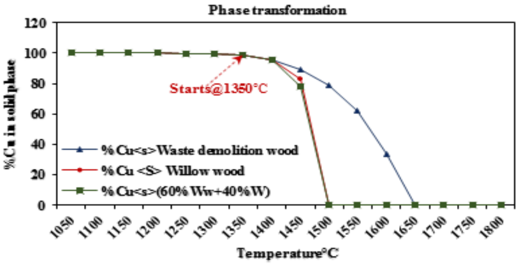
The predicated solid-gaseous phase transitions of As, Cr, and Cu during BR are depicted in Fig.9. (a, b, and c), and quite obviously each element remains (about 100%) in solid phase.



a % As phase transition

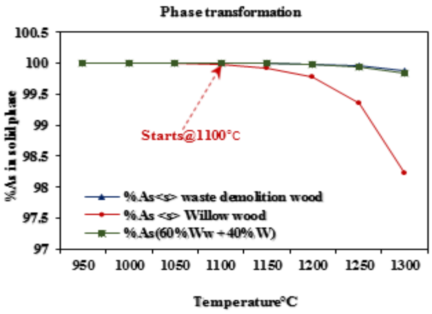


b) %Cr phase transition

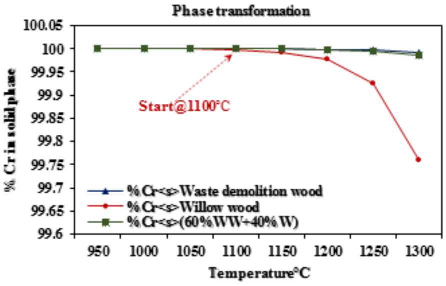


c) % Cu phase transition

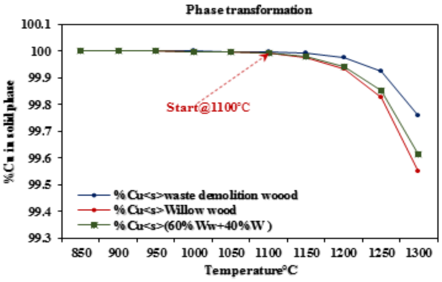
Fig. 8.The transformation behaviour of As, Cr, and Cu-elements in demolition wood, and feed stock -willow wood and wood mixed :(%60 waste demolition wood (Ww) with %40 willow wood (W)) ;under PCR gasification atmosphere (1atm) at temperature between 0-1800 (°C).



a) % As phase transition



b) %Cr phase transition



c) % Cu phase transition

Fig. 9.The transformation behaviour of As, Cr, and Cu –elements in demolition wood, and feed stock -willow wood and wood mixed ;(%60 waste demolition wood (Ww) with %40 willow wood (W)) ;under BR gasification atmosphere (1atm) at temperature between 0-1300 (°C)

IV. CONCLUSION

In this paper, the partial combustion reaction (PCR) and boudouard reaction (BR) of gasification are modelled to study the behaviours of As, Cr, and Cu present in willow wood, demolition wood, and a mixture comprises these two types of wood. The refined results of PCR show that solid-gaseous phase transition of As, Cr, and Cu present in willow wood increased approximately by 150 (°C), 250 (°C), and 250 (°C) respectively, comparing to those obtained under BR. And also solid-gaseous phase transition of As and Cr under PCR decreased about 150 (°C) and 250 (°C), comparing to those obtained under the same reaction when demolition wood was used. Furthermore, the results obtained by gasification of the blended woods reveal improvement in the phase transformation temperature of As and Cr about 150 (°C) and 100 (°C), respectively, comparing to those obtained under PCR when willow wood was gasified. As a consequence, the carried out work proved that systematically mixing of different types of waste woods can return potential advantages over the gasification of single type. It follows that utilising the waste wood contamination for clean energy production, specifically PCR of gasification, and disposal of waste woods.

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