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ВАЛОРИЗАЦИЯ ФРУКТОВЫХ ОТХОДОВ: ЧИСЛЕННЫЙ ПРОГНОЗ СОСТАВА ПРОДУКТОВ ГАЗИФИКАЦИИ

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В работе с использованием вычислительной техники исследуются различные виды фруктовых отходов, чтобы предсказать продукты их газификации при воздействии более высоких температур, а именно 800 °С и 900 °С. Из различных опубликованных источников были собраны результаты предварительного и окончательного анализа восьми различных видов отходов фруктов, а также рассчитана степень газификации методом минимизации свободной энергии Гиббса к каждому отходу в отдельности и к обеим температурам с помощью функции Solver Tool в Microsoft Excel. В качестве исходных данных для моделирования были необходимы термодинамические константы для каждого газообразного компонента и элементный анализ кожуры каждого фрукта. Предсказанный газовый состав был сопоставлен с литературными данными, определено, что он находится в близком соответствии и укладывается в среднеквадратичную ошибку. Это было сделано с учетом частичной конверсии углерода во время газификации.

Ключевые слова: газификация, свободная энергия Гиббса, термодинамические постоянные, среднеквадратическая ошибка, сравнение

VALORIZATION OF WASTE FRUIT PEELS: A COMPUTATIONAL STUDY ON PREDICTION OF GASIFICATION PRODUCT COMPOSITION

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In this work, a variety of discarded fruit peels are investigated using a computational technique in order to anticipate the products of their gasification when subjected to higher temperatures, namely 800°C and 900 °C. The proximate and ultimate analyses of eight different fruit peels

were collected from a variety of published sources, and the composition of gasification was predicted by applying the Gibbs free energy minimization method to each fruit peel individually and to both temperatures using the Solver Tool feature of the Microsoft Excel Spreadsheet. As input for the simulation, the thermodynamic constants for each gaseous component and the elemental analysis of each fruit peel were needed. The predicted gaseous composition was compared with some of the data obtained in the literature, and it was determined to be in a close match based on the root mean square error for each number. This was done while taking into account the fact that the carbon conversion process during gasification was only partially successful.

Keywords: gasification, proximate, ultimate, Gibbs free energy, thermodynamic constants, root mean square error, conversion

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INTRODUCTION

The unprecedented exploitation of traditional sources has made the conversion of biomass into energy and other byproducts an absolute need in today's world. As a result, almost all of the biomass ought to be changed into consumable forms of energy and gaseous products that may be burned. The term "biomass" refers to a variety of waste products, including agricultural and forest leftovers, as well as waste products from households and companies, such as the fruit peels that are produced by industries that process fruit. For the purposes of this research, the peels from eight distinct kinds of fruits are categorized as various forms of biomass to be converted into gaseous products. Biological and thermal processes are only two examples of the many ways that biomass may be transformed into usable forms of energy and other byproducts. Combustion, pyrolysis, and gasification are all examples of thermal techniques; nevertheless, each of these processes requires a unique set of operating conditions and, as a result, generates an entirely unique product composition. These procedures have previously been described in some other location [1] in considerable length. However, the potential advantages of gasification over other processes include the possibility of combining the operating temperature, the equivalence ratio, and the features of the specific reactor, such as fixed / fluidized / entrained bed / vertical shaft / moving grate furnace / rotary kiln / plasma reactor, etc., that can produce a mixture of combustible gases [2], also known as syngas. Syngas is a mixture that mostly consists of hydrogen and carbon monoxide, with some small amounts of methane.

Heating in a gaseous medium such as air, oxygen, steam, or a mix of these with inert gases is the method that is used in gasification, which is one of the promising technologies that turns various kinds of wastes and biomass into valuable products such as bio-oil and combustible gases. Gasification is one of the technologies that has a lot of potential. Combustible gases are produced as a byproduct of the process, which turns the intrinsic chemical energy of the carbon that is contained in the biomass. During the process of gasification, several other reactions take occur at the same time, such as the water shift gas reaction. This reaction may take place at lower temperatures as well as higher temperatures, with or without a catalyst [3]. As a result, the gasification process may be divided into two categories: homogeneous and heterogeneous. Many researchers, including Hiteshue et al., have built and investigated a wide variety of gasifiers that are utilized for the gasification of various forms of biomass. Authors from another research [4] created a gasifier with two stages in order to facilitate the gasification of carbon particles. Pindoria et al. [5-7] then changed this concept on a laboratory scale to generate tar in the pyrolysis part and then crack that tar in the gasification stage using a catalyst. This was accomplished by modifying this design. Details of an additional change to the reactor design for tar cracking may be found elsewhere in the body of published work [8, 9].

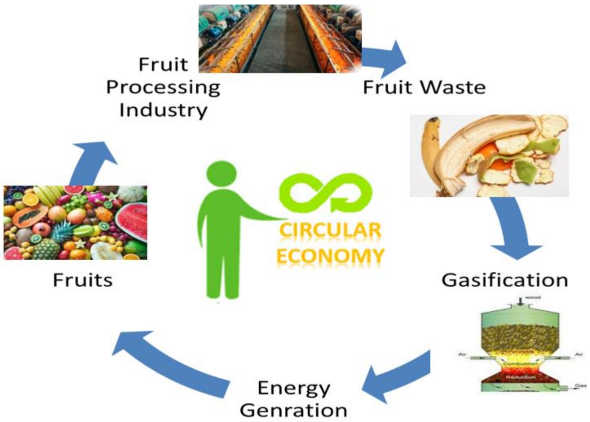

Fig. 1. Circular economy for fruit gasification process
Рис. 1. Экономика замкнутого цикла процесса газификации фруктов

According to the findings of earlier studies [9], there are a variety of methods and tools that may be used for modeling and simulation of gasification experimental data of a broad variety of biomass. These methods and tools are able to forecast the composition of gaseous products. The study was focused on predicting the gas composition of the product by applying the Gibbs free energy minimization approach while taking into account municipal solid wastes. It was thought that the gasification of the municipal solid waste occurred at several temperatures, including 600, 700, 800, and 900 degrees Celsius. During the course of the simulation, both full and partial carbon conversions were taken into consideration. In order to construct, simulate, and ultimately optimize the conditions of the gasification process, a variety of models were built [9]. These models took into consideration the many different kinds of reactor designs, biomass, catalysis, operating conditions, and many other aspects. In addition, a variety of thermodynamic, equilibrium, kinetic, artificial neural network, and other models as well as tools for analysing the gasification process were discussed in the relevant literature [9].

On the other hand, it was found that there is no literature about the gasification of various kinds of fruit peels. These are the solid wastes that are generated by fruit manufacturing enterprises and juice retailers. In the course of this study, the peels of several fruits were evaluated with the purpose of determining the gasification process that they underwent. Fruit peels that have been thrown away are a source of biomass that, when put through a gasification process, may be transformed into gaseous products that are both efficient and beneficial.

This study is predicated on the modeling of the gasification process, which will determine the product composition under a variety of temperature settings.

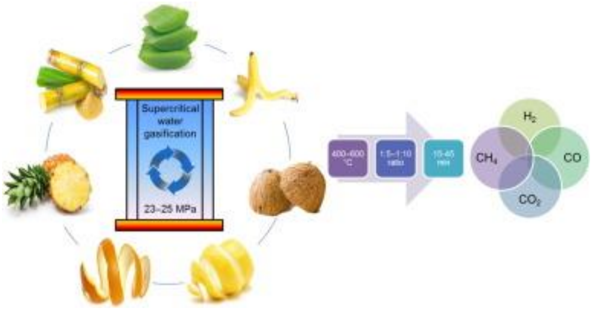

Fig. 2. Gasification process and its products
Рис. 2. Процесс газификации и его продукты

Additionally, it is predicated on proximal and final analysis of waste fruit peels. In the previous study [9], the authors outline the thermodynamic model that is more favourable for minimization of the Gibbs free energy than the equilibrium model. This is because it does not need the specification of a chemical process in order to identify the solution. The overall Gibbs free energy of the system is minimized using this approach when it is in the equilibrium state. The Gibbs free energy of each element at a certain temperature is calculated using its standard enthalpy and entropy, which are finally determined using its thermodynamic coefficients [10]. During the process of biomass gasification, it was thought here that the conversion of carbon was only partially successful. This hypothesis is supported by findings from earlier investigations [9].

METHODOLOGY

In this work, the Gibbs free energy minimization approach was used to simulate experimental data in order to forecast the gasification products of a variety of discarded fruit peels when the temperatures were increased to 800 and 900 °C. In this study, the following waste fruit peels were utilized: orange peel, banana peel, lemon peel, jackfruit peel, citrus fruit peel, pomegranate peel, pineapple peel, and watermelon peel. The ultimate and proximate analyses of these waste fruit peels were collected from various literatures [11-13] and are presented in table 1.

THERMODYNAMIC MODELING

Mathematical modeling for the number of moles of gases formed by gasification process is carried out taking the assumption of complete carbon conversion as well as incomplete carbon conversion, since the conversion of carbon in gasification process will affect the quality and quantity of final gaseous product. In the model, the tar produced is also taken into consideration, assuming $C_{10}H_8$ as tar component. The important thing of the model is that it considers all the possible reactions taking place during gasification at equilibrium. General chemical reactions taking place in gasification process are given in Table 2 [9].

Table 1. **Proximate and ultimate analyses (weight %) of various fruit peels**

Таблица 1. **Приблизительный и окончательный анализы (вес. %) отходов различных фруктов**

Biomass	C	H	O	N	S	Volatile Matter	Moisture	Fixed Carbon	Ash
Orange Peels [11]	39.7	6.2	53	0.46	0.6	77.73	9.2	13.07	2.94
Lemon Peels [12]	40.33	5.96	52.25	1.27	0.19	87.16	6.1	1.34	5.4
Banana Peels [12]	40.24	6.14	52.22	1.3	0.098	85.26	9.8	0.07	5.01
Citrus Peels [12]	38.51	6.2	54.55	0.64	0.1	86.54	7.58	1.56	4.32
Jackfruit Peels [12]	40.04	5.86	53.08	0.9	0.12	86.28	6.48	0.92	6.32
Pomegranate Peels [13]	35.96	4.92	58.38	0.65	0.09	85.68	10.43	0.25	3.63
Pineapple Peels [13]	36.46	6.01	56.28	1.07	0.18	83.77	8.86	0.83	6.55
Watermelon peels [13]	39.69	6.23	51.52	2.23	0.33	85.36	8.19	0.27	6.18

From all these reactions, the water-gas reaction, hydrogasification and Boudouard reactions are of highest importance as these reactions favor the formation of the main components of the syngas i.e. carbon monoxide, hydrogen and methane. If complete carbon conversion is considered, the major outputs from the process would be CO, CO_2, H_2, CH_4 and H_2O. The N_2 is a significant component in the case of air gasification. Therefore, the overall reaction considered on the basis of proximate analysis of the sample [14] is:

$$CH_mO_pN_qS_r + aH_2 \rightarrow CO + CO_2 + CH_4 +$$
$$+ H_2 + H_2S + C_{10}H_8(tar) + N_2 + H_2O$$

Here, the average molecular weight of tar produced is considered equivalent to the molecular mass of naphthalene $C_{10}H_8$. The total Gibbs free energy of the system is defined as the summation of product of number of moles and chemical potential of each species.

$$G^t = \sum_{i=1}^{N} n_i\, \mu_i \qquad (1)$$

Here, G^t is the total Gibbs free energy and n_i is the number of moles of species i and μ_i is the chemical potential of species i, given by

$$\mu_i = \Delta\overline{G_{f,i}^{o}} + RTln(y_i) \qquad (2)$$

In equation (2), y_i is the mole fraction of gas species i and it is the ratio of n_i and the total number of moles in the reaction mixture (n_{total}). The $\Delta G^o_{f,i}$ is the standard Gibbs free energy of formation of species i, and it is set equal to zero for all chemical elements.

Substituting equation (2) into equation (1), we get

$$G^t = \sum_{i=1}^{N} n_i\, \Delta\overline{G_{f,i}^{o}} + \sum_{i=1}^{N} n_i\, RTln\left(\frac{n_i}{n_{total}}\right) \qquad (3)$$

Let equation (3) is the objective function which is to be minimized, in which the values of n_i must be known. For the minimization of the Gibbs free energy problem, the method Lagrange multiplier [9] can be used.

The constraint of this optimization problem is the elemental balance, i.e.

$$\sum_{i=1}^{N} a_{ij}\, n_i = A_j \qquad (4)$$

Here, $j = 1, 2, 3, \ldots., k$ and a_{ij} is the number of atoms of the j^{th} element in a mole of the i^{th} species. A_j is defined as the total number of atoms of the j^{th} element in the reaction mixture. To form the Lagrangian function (L), the Lagrange multipliers, $\lambda_j = \lambda_1, - - -, \lambda_k$ are used by multiplying with elemental balance constraints, and those terms are subtracted from G^t.

$$L = G^t - \sum_{j=1}^{k} \lambda_j \left(\sum_{i=1}^{N} a_{ij}\, n_i - A_j\right) \qquad (5)$$

The partial derivatives of equation (5) are set equal to zero in order to find the optimum value.

$$\left(\frac{\partial L}{\partial n_i}\right) = 0 \qquad (6)$$

Above equation (6) can be formed in terms of a matrix to create a set of non-linear simultaneous equations that has i rows and those are solved by an iteration technique with the constraints as defined in equation (5). However, the solutions n_i have to be real numbers in the boundary condition that $0 \le n_i \le 6\ n_{total}$.

In order to calculate the standard Gibbs free energy of each chemical species at specific temperature T, $\Delta G^o_{f,i}(T)$, the values of the standard enthalpy of formation, $\Delta H^o_{f,i}(T)$, and the standard entropy of formation, $\Delta S^o_{f,i}(T)$ at temperature T are required since

$$\Delta\overline{G_{f,i}^{o}} = \Delta\overline{H_{f,i}^{o}} - T\Delta\overline{S_{f,i}^{o}} \qquad (7)$$

The data from the Technical Memorandum number 4513 [10], is used to calculate the standard enthalpy of formation and standard entropy of formation. From this data source, the heat capacity at constant pressure for a standard state was formulated in a polynomial equation of order four with five constants (a_1, a_2, a_3, a_4, a_5) as follows.

$$\frac{\overline{C_p}(T)}{R} = a_1 + a_2T + a_3T^2 + a_4T^3 + a_5T^4 \qquad (8)$$

For the enthalpy and the entropy, they are defined in polynomials with six constants (a_1, a_2, a_3, a_4, a_5, b_1 / b_2) as follows.

$$\frac{\overline{H^o}(T)}{RT} = a_1 + a_2\frac{T}{2} + a_3\frac{T^2}{3} + a_4\frac{T^3}{4} + a_5\frac{T^4}{5} + \frac{b_1}{T} \qquad (9)$$

$$\frac{\overline{S^o}(T)}{R} = a_1 lnT + a_2T + a_3\frac{T^2}{2} + a_4\frac{T^3}{3} + a_5\frac{T^4}{4} + b_2 \quad (10)$$

The arbitrary base selected for calculating the enthalpy value for all species is zero at 298.15 K in the case of reference elements and gaseous compounds. Thus,

$$\Delta\overline{H_f^o}(298.15) = \overline{H^o}(298.15) = 0 \quad (11)$$

The enthalpy of formation in equation (9) can be computed by following the definition that it is the enthalpy change occurring when a compound is formed stoichiometrically from its stable elements at temperature T.

$$\Delta\overline{H_f^o}(T) = \overline{H}^o_{comp}(T) - \sum_{i=element}\left(v_i\overline{H}^o(T)\right) \quad (12)$$

where v_i is the stoichiometric coefficient for element i. The thermodynamic coefficients required for calculation were taken from Technical Memorandum 4513 [10], for the operating temperature < 1000 K and for > 1000 K. The values of all the thermodynamic coefficients can also be taken from our previous literature [9].

Previous research [9] provides a thorough explanation of the equilibrium model that was used in this investigation. This model was used to investigate the impact that temperature has on the equilibrium reaction state as well as the chemical make-up of the products of gasification. The model consists of the system's total Gibbs free energy, which is equal to the summation of the product of the number of moles and the chemical potentials of each species when those potentials are examined in the context of the overall reaction. The standard Gibbs free energy of formation of each species and the standard ole percentage of each gaseous species are added together to arrive at the chemical potential of each species. Consequently, the total Gibb free energy is constrained to be minimized by the Lagrange multiplier approach in order to satisfy the requirements of elemental equilibrium for each species. The Solver feature in Microsoft Excel's worksheet is used to solve all of the non-linear simultaneous equations that were thus produced. In order to compute the standard Gibbs free energy for each species at a given temperature, one must first get the standard enthalpy and standard entropy of each species from the relevant research [15-19].

SIMULATION

In order to simulate employing equilibrium modeling, a spreadsheet created in Microsoft Excel was used. It was expected that every fruit peel would gasify between 800 and 900 degrees Celsius. The Gibbs free energy was minimized with the help of a solver tool since the approach for doing so is an effective method of optimization that can be used with a variety of constraints. The solver tool makes simultaneous use of the Lagrangian and generalized reduced gradient optimization approaches in order to get optimal results. During the simulation, the following notations were taken into consideration: N1 for carbon dioxide, N2 for carbon monoxide, N3 for hydrogen, N4 for methane, N5 for hydrogen disulfide, N6 for nitrogen, N7 for water, and N8 for tar ($C_{10}H_8$) components. In a prior research [9], it was presumed that the carbon conversion was either completely or partially carried out. However, the only assumption that properly reproduced the data under consideration was the assumption of incomplete carbon conversion, which resulted in a root mean square error that was much lower than that of the experimental data. The following is a list of the general stages that are taken while optimizing anything.

1. Operating temperature T under consideration, proximate analysis, and thermodynamic coefficients of each possible gaseous component and each chemical element including C, H, O, N, S are inputted in the excel sheet.
2. Minimization of Gibbs free energy method is applied to calculate n_i.
3. Energy balance equation is applied to calculate DG^t.
4. If DG^t was found less than 10^{-5}, then above steps are repeated from step 2.

RESULT & DISCUSSION

Using the MS-Excel Solver Tool and the presumption of an incomplete carbon conversion, the analytical data of eight different discarded fruit peels that were found in the literature [11-13] was simulated. At two distinct temperatures, a model was developed to predict the chemical make-up of the gaseous product that results from the gasification of these fruit peels. Table 2 presents the results of the results of the consequent anticipated values of product gas composition on a volume basis at temperatures of 800 and 900 °C. It demonstrates that an increase in the operating temperature leads to an increase in the generation of carbon monoxide and hydrogen in the majority of situations. Nevertheless, when the temperature rises, there is a minor reduction in the amount of methane that is formed. At temperatures of 800 and 900 °C, it has been discovered that each of the eight fruit peels retains around one percent of its original carbon content in the form of ash.

Table 2. **Predicted gaseous products composition from eight different fruit peels**

Таблица 2. **Прогнозируемый состав газообразных продуктов из отходов восьми различных фруктов**

Species	Banana		Lemon		Citrus		Jackfruit	
	800 °C	900 °C	800 °C	900 °C	800 °C	900 °C	800 °C	900 °C
CO_2	14.31	13.58	13.00	13.39	15.76	16.06	13.60	13.72
CO	34.40	34.80	37.41	36.02	32.00	31.23	37.18	36.33
H_2	21.26	30.65	21.72	29.75	23.09	32.56	21.22	29.49
CH_4	16.53	11.23	15.65	11.07	15.05	10.09	15.27	10.73
H_2S	0.07	0.20	0.14	0.20	0.13	0.28	0.20	0.19
N_2	1.06	0.89	0.60	0.90	0.51	0.48	0.73	0.69
H_2O	11.28	7.50	10.50	7.50	12.58	8.29	10.86	7.75
$C_{10}H_8$	1.08	1.15	0.98	1.16	0.86	0.98	0.94	1.09
Species	Pomegranate		Pineapple		Orange		Watermelon	
	800 °C	900 °C	800 °C	900 °C	800 °C	900 °C	800 °C	900 °C
CO_2	21.26	23.02	16.89	17.65	14.23	14.24	13.78	11.30
CO	30.93	28.35	30.18	29.20	34.58	33.87	34.62	36.56
H_2	20.38	28.30	23.03	32.15	21.81	31.17	21.49	29.77
CH_4	11.47	8.53	13.22	9.06	16.27	11.03	17.22	11.54
H_2S	0.46	0.20	0.13	0.13	0.45	0.42	0.25	0.13
N_2	0.41	0.71	0.86	0.81	0.37	0.35	0.67	0.84
H_2O	14.27	9.96	14.92	10.17	11.38	7.84	11.03	8.84
$C_{10}H_8$	0.81	0.91	0.76	0.83	0.90	1.07	0.94	1.02

DECLARATIONS

Ethical Approval: Ethical approval was not required for this study, as it did not involve any human participants or the use of human data.

Competing Interests: The authors declare that they have no competing interests.

Authors' Contributions: Conceptualization & writing: Dr. Ruta Khonde; Interpretation & review: Dr. Rohit Khedkar; Analysis & editing: Dr. Pawan Meshram.

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Availability of Data and Materials: The data and materials used in this study are not publicly available, but are available upon request from the corresponding author.

We confirm that the manuscript has been read and approved by all named authors and that there are no other persons who satisfied the criteria for authorship but are not listed. We further confirm that the order of authors listed in the manuscript has been approved by all of us.

The authors declare the absence a conflict of interest warranting disclosure in this article.

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