THERMODYNAMICAL DECOMPOSING OF BIOMASS (SHELLS OF WALNUT, HAZELNUT AND COMMON REED) WITH THE USE OF CONCENTRATED HEAT OF SOLAR RADIATION

K.D. Sultanova, P.F. Rzayev, A.A. Garibov, R.M. Mustafayeva, O.M. Salamov

Institute of Radiation Problems of the Azerbaijan National Academy of Sciences,
Baku, AZ-1143, H. Javid avenue-31a, phone/fax : + (994 12) 439-83-18,
e-mail: kemale-sultanova@rambler.ru, rzayev-pf@yahoo.com

ABSTRACT

This paper is devoted to the investigation of thermodynamical decomposing of biomass (shells of walnut-fruited goods of forest). With purposes of enhancing of assortment of biomass in the process of obtaining of energy-intensive energy carriers, common reed is used as non-cultivated high-productive plant. Common reed occupies in the Republic, and particularly in Absheron Peninsula, areas equal to 78000 and 1425 hectares, consequently. It is possible to get from 4 to 6 m^3 gas from the area of one hectare occupied by common reed. Systematic and purposeful use of these wastes undoubtedly promises significant economical and ecological effects.

Key words: *biomass, walnut, hazelnut, common reed*

1. INTRODUCTION

Continuous increase of oil and natural gas prices (currently proved and explored resources of oil and gas in the republic are equal to ~ 2 billion tones and 5.7 trillion m^3, consequently) in combination with real expected exhaustion of their resources in the near future (within 30-50 years) puts a task for scientists of the Republic of Azerbaijan on intensive search of new and "clean" energy sources. One of them is the biomass of "waste products" - products of forest, shells of walnut and hazelnut. Application of high-potential heat of solar radiation (about $500 \div 700^0$C) will allow obtaining of both gaseous and liquid fuel by means of thermal-chemical decomposition of biomass in the presence of oxidant. Application of solar energy in this case will allow saving up to 40 % of the traditional fuel usually used in the considered process.

Resources of nut cultures are available practically in all areas of the Republic. They are especially significant in Sheki-Zagatala zone where more fault in supply of the population by natural gas and by the electric power is observed (Tables 1 and 2).

Table 1. Production of nut cultures in the country

Name	Gases				
	$\frac{area\ (hectare)}{production\ (m^3)}$				
	2000	2001	2002	2003	2004
Walnut fruits	2547.7 9983	2560 9208	2722 8827	2818 9701	2842 4335
Hazelnut fruits	18350.3 13334	185270 15945	19111 16120	19472 19825	19900 5991

Table 2. Territorial distribution of nut-production zones in the Republic (ha) and their production for a year (t)

Territory	Area, ha	Production, t/year
Nakhchivan Autonomous Republic	290,2	2399
Sheki-Zagatala	928	18025
Guba-Gusar	809	1145
Gazakh-Ganja	288	779

Under industrial conditions at their processing into high-quality products – the oil, the walnut shell and shell of hazelnut, averaging up to 55% of weight of the initial product, is formed in the form of waste. These wastes, as well as common reed wastes are desirable, by the use of concentrated solar energy, to transform into valuable and useful products and chemical energy carries.

Perspective accessible raw material in this aspect as it has been shown above is the high-yielding raw material – common reed.

Common reed (*Spirpus*) is a grassy plant of sedgy family (in Azerbaijan known as *Gil*) being perennial, less often, annotinous grass. The lake common reed (S.Jacustvis) with cylindrical, almost leafless stalks (caulis) with heights up to 2.5 m is most known one in the country.

Creeping rhizomes promote its distribution and forms strong networking cover at the bottom of shallow water reservoirs. The common reed always grows in water or directly at coast on depth of 3-5 m forming dense tangles with wide belts going deep into a reservoir behind a zone of a cane. Together with a cane the common reed promotes overgrowth of lakes.

In the leach of aboveground part of a common reed it contains 0.10 P_2O_5, 0.22 CaO, and 2.72 SiO_2.

At burning a rhizome in ashes it is found out: 0.10 % CaO, 0.55% P_2O_5 – 0.09 K_2O.

The amount of ashes which remains after burning makes 1.4 tones/hectare.

In comparison with other artificial fertilizers the leach of a common reed favorably differs from other used fertilizers with the fact that it contains many substances necessary for plants: nitrogen, phosphorus, calcium and manganese

The further works on expansion of assortment of carbon - containing substances, along with shells of walnut and hazelnut, in addition also common reed, and possibly in the future also common reed, will allow to save traditional fuel as well as also to obtain valuable products (energy carriers, fertilizers, etc.).

One of such products which obtaining can be based on use of a shells of walnut, hazelnut and common reed is the charcoal which output at the temperature ~ 500^0C makes accordingly 34.5 and 26.3 % from the initial shot (weight) [1, 2].

II. EXPERIMENTAL INVESTIGATIONS

During pyrolysis process in high-temperature solar energetic plant which includes units of system of delivering and dosing of raw material, heliogasgenerator, systems of orientation to the Sun and gathering of formed gas, blocks of guidance and the control of technological process, it was used the crushed raw material of fraction (1.0÷2,5 mm), preliminary dried up to constant weight at temperature 105^0C.

Then the amount of 100 gram was loaded in the heliogasgenerator of solar energetic plant. Heliogasgenerator was placed in focal area of the solar furnace where for adjustment of temperature by means of the special mechanism (nonius or vernier), moving heliogasgenerator along a focal axis of a mirror (forward-back) optimum temperature of process was achieved.

Pyrolysis of considered raw material was carried out at temperature (200÷700^0C) before the termination of excretion of liquid (up to 500^0C) and gaseous products (~700^0C). Upon termination of technological process, weighing of a flask was made on electronic weights.

Elementary and chemical compound H/C, O/C and calorific (heating) ability of walnut and hazelnut shells and common reed were determined (Tables 3 and 4).

Taking into account data of element analysis (Table 4), the high calorific ability of charcoal was determined according to the data [2] which is provided in the Table 4 as well.

Table 3. Chemical compound of shell of walnut, shell of hazelnut and common reed from the initial raw material

Components, %	Shells		Mass
	Walnut	hazelnut	Common reed
Liginin	52.0	45.5	41.5
Hemicelluloses	4.6	9.5	9.2
Celluloses	34.6	24.97	39.3
Water-soluble substances	6.5	9.9	6.2
Cindery substances	0.8	1.27	0.8
Fats and pitch	3.2	1.5	1.2

Table 4. The data of the element analysis of H/C, O/C and calorific value of the charcoal received from walnut shell, hazelnut shell and common reed

Name	C	H	O	N	H/C	O/C	High calorific value, kcal/kg
Hazelnut shell	51.5	5.2	43.2	0.2	1.21	0.63	4384
Walnut shell	52.0	7.3	40.7	0.2	1.68	0.59	4498
Common reed	49.6	6.3	41.2	0.58	1.18	0.42	3263

With the help of experimental investigations in solar energetic plant a pyrolysis of walnut shell, hazelnut shell and then stalks of common reed was carried out.

The obtained data is provided in the Table 5.

A structure of formed gas at pyrolysis from a walnut shell, hazelnut shell and common reed are provided in the Table 6.

Table 5. Output of charcoal from walnut shell, hazelnut shell and common reed

Pyrolysis temperature	Consumption of charcoal, % from weight		
	Walnut shell	Hazelnut shell	Common reed
100^0C	100	100	100
200^0C	95.2	94.4	86.2
300^0C	44.5	42.8	30.3
400^0C	36.0	35.4	18.0
500^0C	34.8	34.0	16.5

Table 6. Structure of gas formed at pyrolysis of walnut shell, hazelnut shell and common reed

Name of sample	500^0C			600^0C			700^0C		
	H_2	CO	CH_4	H_2	CO	CH_4	H_2	CO	CH_4
Hazelnut shell	19	12	4.6	65	17	6.0	68	15	7.0
Walnut shell	18.5	12.8	5.0	64.2	16.6	6.5	66	14	8.0
Common reed stalks	16.0	9.6	8.4	52.5	14.5	7.3	54.3	12.5	9.2

The analysis of Table 6 shows that the structure of obtained gas at thermal decomposition of walnut shell, hazelnut shell as well as common reed strongly depends on temperature of pyrolysis. For example at 500^0C it is obtained a gas containing relatively small amount of H_2 CO and CH_4 and heavy hydrocarbons. At high temperatures, at ~ 700^0C, there is more output of H_2 and less - CO and CH_2.

With purposes of intensification of gas-making process, a calculation of kinetic characteristics of process was made on the base of following relations [3, 4]:

$$C + H_2O \rightarrow y_1CO + y_2H_2 + ... \qquad (1)$$

$$A + B = C + D \qquad (2)$$

$$V = k \cdot C_{A_1}^{n_1} \cdot C_{A2}^{n_2} \cdot C_{A_3}^{n_3} ... C_{An}^{n_n} \qquad (3)$$

$$n_{oA_1} \cdot \frac{dx}{Sdt} = k \cdot C_{A_1}^{n_1} \cdot C_{A2}^{n_2} \cdot C_{A_3}^{n_3} ... C_{An}^{n_n} \qquad (4)$$

$$V = \frac{\sum n_i RT}{P} \qquad n_{A_i} = n_0 A_i (1-x)$$

$$C_{A_i} = \frac{n_{A_i}}{V} = \frac{n_0 A_i (1-x) P}{\sum n_i RT} \qquad (5)$$

$$\frac{dx}{dt} = K \frac{SP^2}{R^2T^2} \cdot \frac{(1-x)(n_{oB} - n_{jB}^x)}{(n_{oA} - n_{OB})} \qquad (6)$$

$$K = \frac{(n_{oA} - n_{OB})^2}{(n_{oA} - n_{OB})} \cdot \frac{R^2T^2}{VP^2} \ln \frac{n_{oB}(1-x)}{(n_{oB} - n_{OA}^x)} \qquad (7)$$

$$K = 4n_{oA} \cdot \frac{R^2T^2}{VP^2} \cdot \frac{x}{(1-x)} \qquad (8)$$

$$t = \frac{PV}{n_{oA} \cdot RT} \qquad (9)$$

where *A* is a charcoal, *B* is a water steam, *C* is a molecular hydrogen, *D* is monoxide of carbon, *V* is speed of chemical reaction, *K* is a constant of speed of chemical reactions, $k \cdot C_{A_1}^{n_1} \cdot C_{A2}^{n_2} \cdot C_{A_3}^{n_3} ... C_{An}^{n_n}$ are concentrations of reacting substances, n_1, n_2, $n_{3...}$ n_n are orders of reaction, *S* is the area of section of heliogasgenerator, $\sum n_i$ is the total number of moles, *x* is the amount of reacted substances A_i at the distance *l* determined from the beginning of the reactionary zone, expressed in fractions from initial amount, *R i*s the universal gas constant, *T* is a temperature, *P* is the general pressure of intermixture of gases.

In connection with identity of technological process for the chosen objects as an example we made calculation of technological process for the walnut shell. Results of calculations are provided in the Tables 7 and 8.

Table 7. Output of gas in gasification of charcoal (from walnut shell) with H_2O at temperature 700^0C

Time, minutes	Consumption, 10^{-3} kg		Output, 10^{-3} m^3	
	H_2O	C	H_2	CO
10	5.28	3.52	6.54	6.60
20	11.13	7.42	13.82	13.85
30	18.56	12.24	22.80	22.84
40	27.66	18.44	34.42	34.38
50	36.63	22.42	41.80	41.76
60	43.74	25.16	46.92	46.90

Table 8. Calculation of kinetic characteristics of gasification process of charcoal with H_2O at temperature 700^0C

Time, minutes	Volume, V 10^{-3} m^3	$N_{OA,}$ mole/min	$C+H_2O=CO+H_2$	
			X	K
10	13.14	0.58	0.087	0.0863
20	27.67	1.24	0.185	0.0506
30	45.64	2.04	0.305	0.0436
40	68.80	3.08	0.461	0.0478
50	83.56	3.91	0.587	0.0486
60	93.82	4.52	0.686	0.0504

The curve describing time changes of constant of chemical reaction speed *K*, drawn on data of Table 8, is shown in Fig.1. The analysis of the obtained curve allows representing of passing of technological process enough precisely.

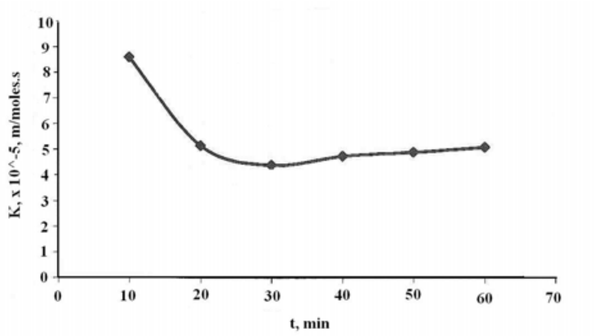

Figure 1

As it is seen from Fig.1, speed of formation of gases (first of all H_2) quickly grows, reaches a maximum, then occur some reduction of outputs of H_2 and CO which then is stabilized. Such reduction of *K* is probably connected to the influence of significant heat losses at high temperatures and at smaller capacities of heliogasgenerator of solar high-potential helio-energetic plant.

III. CONCLUSION

The given method of calculation, in our opinion, can be used with success at calculations of similar and more powerful helio-energetic complexes.

REFERENCES

1.*K.D.Sultanova, N.I.Eyyubova, P.F.Rzayev, V.R.Rustamov.* Possibilities of utilization of shells of nut-bearing cultures for obtaining of fuel gas. Fifth Baku International Congress "Energy, Ecology, Economy", Baku, Azerbaijan Republic, 21-24 September 1999, pp.89-95.

2. Biomass as a source of energy. (Translated from English, Eds. S.Soyfera, O.Zaborski). Moscow, PH "Mir", 1985 (in Russian).

3.*E.D.Levin.* Theoretical fundamentals of production of charcoal. Moscow, PH "Lesnaya Promyshlennost", 1980, 150 p. (in Russian)

4. *V.N.Kondratev.* Kinetics of chemical gas reactions. Moscow, PH of USSR Academy of Sciences, 1988, 450 p. (in Russian).