Andrzej Mitura*

RESEARCH OVER THE INFLUENCE OF ENERGETIC MIXTURE COMPOUNDS ON COMBUSTION HEAT**

1. Introduction

The co-firing of conventional fuels with substitute fuels like in energetic boilers installations is conducted in many energy units in the whole world [1]. Many parameters are decisive about possible applications of certain product as a fuel. These are factors which influence the possible application of the product dependably on the conditions within certain installation where the fuel should be directed. One of the criteria being evaluated and influencing the fuel quality is combustion heat [2]. The research over fuel mixtures of various shares of individual components was performed and the their combustion heats were determined. The paper describes the attempt of evaluation of combustion heat change dependably on the change of two components in four components fuel mixture. This mixture was produced on the basis of four wastes and the direction of their application is in accordance to assumptions of National Planning of Wastes Utilization and plans created for individual voivodships [3]. The conducted investigations may cause the elimination of such places as deposits of coal slimes or deposits of carbon black by its utilization [4].

2. Analysis of obtained results

The series of experiments were conducted in which the shares of oil and carbon black were changed. To fully recognize the possibilities of applying the proposed calculation method

^{*} AGH University of Science and Technology, Krakow

^{**} The research was financed from scientific project no 15.11.100.624. The author would like to thank prof. Tadeusz Tumidajski for his help during preparation of this paper.

as the continuation of the conducted work the conduction of further works is planned for various shares of other wastes as coal slimes and wood shavings. The preparation of samples of fuel mixtures was based on precise integration of individual wastes-substrates. The representative samples were collected which were then dried and unified for further chemical analyzes.

TABLE 1

The results of analyzes of combustion heat of mixtures by various share of oil and carbon black

No.	Experiment series	Oil	Carbon black	Coal slime	Wood shavings	Q _s , [J/g]	Q_s^t , $[J/g]$
1		10	10	10	10	1 157 800	1 191 950
2	1	15	10	10	10	1 401 705	1 413 925
3	1	20	10	10	10	1 609 500	1 635 900
4		25	10	10	10	1 785 245	1 857 875
5		10	15	10	10	1 313 460	1 354 560
6	2	15	15	10	10	1 668 450	1 576 535
7	2	20	15	10	10	1 844 315	1 798 510
8		25	15	10	10	2 063 280	2 020 485
9		10	20	10	10	1 483 600	1 517 170
10	3	15	20	10	10	1 667 985	1 739 145
11	3	20	20	10	10	1 988 280	1 961 120
12		25	20	10	10	2 200 510	2 183 095
13	4	10	25	10	10	1 612 050	1 679 780
14		15	25	10	10	1 928 460	1 901 755
15		20	25	10	10	2 196 155	2 123 730
16		25	25	10	10	2 338 070	2 345 705

where: Q_s — total combustion heat; Q_s^t — theoretical global combustion heat.

The series 1 characterize by the equal share of carbon black, coal slime and wood shavings and changeable amounts of oil from the range 10–25 units. The elaborated oil contains relatively high contents of sulfur — 0.33% which is the highest amount among all researched wastes as well hydrogen contents of 13.2% and above 85% of element C. The higher amount of oil in the mixture does not influence the growth of discrepancy between total combustion heat and theoretical total combustion heat.

By proportional growth of oil share in series 1, next experiments characterize also by growth of carbon black share from 10 to 15 units in series 2, to 20 units in series 3 and to 25 units in series 4 what in consequence influenced the discrepancies between values of Q_s i Q_s^t .

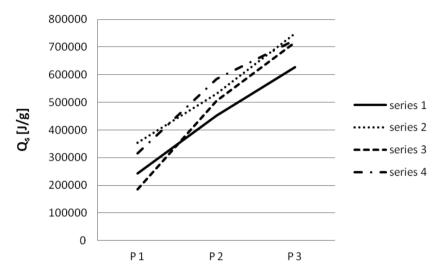


Fig. 1. Change of the value of Q_s according to the change of oil contents in investigated experimental series; P1, P2, P3 — points presenting the value of Q_s for the series of experiments according to the Table 1

Series presented in Figure 1 presents the growth of combustion heat because of the change of oil contents in the mixtures. Series 1 presents the linear growth of combustion heat together with the growth of the oil share in the mixture from 25% to 45% by constant contents of the rest of ingredients. The growth of combustion heat was measured as 54%. Series 2 presents the growth of combustion heat with growth of carbon black share from 10 to 15 units and percentage share of oil within the range 22% till 42%. The growth of combustion heat was equal to 57%. The increase of combustion heat in both first and second series is linear and its course is proportional. The courses of combustion heats growth for series 3 and 4 are similar and because of the similar share of oil (in series 3 — 38% and in series 4 — 36%) the lines approach themselves in point P3. The growth of combustion heat for series 3 was equal 48% and for series 4 — 45%.

The presented courses of combustion heats growth in Figure 2 presents the effect of change of carbon black contents on heat growth in four mixtures. The graphs were elaborated on the basis of combinations created according to Table 1. The constant amount of oil and various share of carbon black within the range 10–25 were accepted for series. On the basis of this graph it is visible that the addition of carbon black less influences the growth of combustion heat. It is less dynamic than in case of oil addition of identical percentage share.

The growths of combustion heat in these series by constant oil contents are as following:

- Series 1, oil contents 10, 39%;
- Series 2, oil contents 15, 38%;
- Series 3, oil contents 20, 36%;
- Series 4, oil contents 25, 31%.

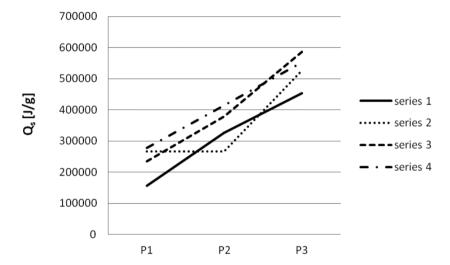


Fig. 2. Change of the value of Q_s according to the change of carbon black contents in investigated experimental series; P1, P2, P3 — points presenting the value of Q_s for the series of experiments according to the Table 1

Less dynamic increase of combustion heat is certainly connected with lower value of carbon black combustion heat and with reactivity of carbon black, which was not measured during investigation. The applied carbon black does not combust with open fire but only glows. To maintain the process it is necessary to deliver energy what makes this reaction as endothermic one and influences the lowering of combustion heat growth in prepared samples.

The elaborated mixtures were prepared with application of four substrates of characteristics presented in Table 2.

The requirements for alternative fuels used by cement plants are as following [4]:

- chlorine contents < 0.3 %,</p>
- sulfur contents < 2.5 %.</p>

As it can be noticed, after comparison of the results for applied substrates none of the requirements is exceeded. In case of the fuel transfer to cement plant it is necessary to investigate the PCB contents and heavy metals contents.

TABLE 2
Results of research of wastes as carbon black, oil, wood shavings and coal slime

Measurement	Unit	Carbon black	Oil	Wood shavings	Coal slime
Analytical moisture	%	1.80	No data	4.00	2.00
Ash	%	2.18	0.8667	0.60	28.21
Total sulfur	%	0.10	0.33	0.01	0.49
Hydrogen	%	2.64	13.20	6.60	3.40
Nitrogen	%	0.38	0.53	0.68	1.01
Chlorine	%	0.11	0.009	0.13	0.35
Total coal	%	90.20	85.60	48.70	57.80
Combustion heat	kJ/kg	32 522	44 395	19 610	22 668

3. Theoretical assumptions of calculating methods

From the point of view of calculating the combustion heat of components mixture this task may be treated as calculation of heat balance introduced by each component. Let mark by m_1 , m_2 , m_3 and m_4 the masses of oil, carbon black, coal slime and wood shavings, respectively and by Q_{s1} , Q_{s2} , Q_{s3} and Q_{s4} their combustion heats. Then by simple balance equation it is obtained that. In this case it is obtained

$$Q_s = m_1 Q_{s1} + m_2 Q_{s2} + m_3 Q_{s3} + m_4 Q_{s4} \tag{1}$$

where Q_s — is theoretical combustion heat of the whole mixture.

The least squared method allow to reproduce this equation if the values m_1 , m_2 , m_3 , m_4 and Q_s are known what means that it is possible to calculate the combustion heats of each component.

On the basis of the data set presented in Table 1 the regressive equation was calculated which is presented in Table 3.

As it is visible, comparing the coefficients of regressive equation for oil and carbon black with the Table 2 indicate that they are equal to combustion heats of the individual components and the absolute term is equal to the sum $10 Q_{s3} + 10 Q_{s4} \approx 422 779$ (the approximation is almost perfect). The statistical characteristics of this equation prove practically the full accordance to the balance equation.

The same calculating procedure was applied for the data determining the real combustion heat of components mixtures and the equation statistically characterized in Table 4 was obtained.

TABLE 3
Characteristics of regressive equation for calculated combustion heat value of the mixture

Variable	Coefficient	Standard error	<i>t</i> -Student value	Significance level p
Const	422779	4,78153	8,842e+04	1,87e-058
Oil	44394,7	0,188455	2,356e+05	5,49e-064
Carbon black	32522,3	0,188455	1,726e+05	3,14e-062

Mean value 1768826 Standard deviation 317731,0 Sum of residual squares 230,8500 Residual standard error 4,213988 Determination coefficient R^2 1,000000 Corrected R^2 1,000000 F(2, 13)4,26e+10 Value of p for test F 1,55e-64

TABLE 4
Characteristics of regressive equation for combustion heat value of the mixture

Variable	Coefficient	Standard error	<i>t</i> -Student value	Significance level p
Const	344780	58085,8	5,936	4,94e-05
Oil	47161,2	2289,35	20,60	2,61e-011
Carbon black	34061,6	2289,35	14,88	1,53e-09

Mean value 1766179 Standard deviation 339239,6
Sum of residual squares 3,41e+10 Residual standard error 51191,36
Determination coefficient R² 0,980265 Corrected R² 0,977229
F(2, 13)322.8676 Value of p for test F 8,30e-12

The obtained coefficients of combustion heats (Tab. 4) differ significantly from their analogues values from the Table 3. It should be concluded then that combined combustion of the components change their thermodynamic characteristics so it causes change of the components role. It should be noticed also that the statistical significance level *p* of the equation from Table 4 is also very low what means that the description given by "new" balance equation is absolutely acceptable.

4. Conclusions

 To optimize the course of further works over preparation of the fuel the combustion heat was selected as the main criterion. This is the value determining the purpose of the fuel preparation and it influences the economic effect connected with application of

- such mixture. The combination of high calorific value with proper fuel parameters as water contents, ash contents are the purposes of actually lasting investigations over the possible pelletizing of prepared mixtures.
- The individual regular growth of the researched factors influences the linear growth of combustion heat value. This trend is identical as for combustion heat calculated theoretically.

REFERENCES

- [1] Soblewski A., Wasilewski R.: Wykorzystanie stałych paliw wtórnych w instalacjach energetycznych. Ochrona Powietrza i Problemy Odpadów, nr 3–4, 2008.
- [2] Wasilewski R., Tora B.: Stałe paliwa wtórne. Górnictwo i Geoinżynieria, Zeszyt nr 4, 2009.
- [3] Krajowy Plan Gospodarki Odpadami 2014 Uchwała Nr 217 Rady Ministrów z dnia 24 grudnia 2010.
- [4] Blaschke W., Baic I., Szaflarczyk J.: Depozyty mułów węglowych źródłem paliwa energetycznego informacja o projekcie rozwojowym. Przegląd Górniczy, nr 1–2, 2010.
- [5] Sarna M., Mokrzyki E., Uliasz-Bocheńczyk A.: Paliwa alternatywne z odpadów dla cementowni doświadczenia Lafarge Cement Polska S.A. Zeszyty Naukowe Wydziału Budownictwa i Inżynierii Środowiska Politechniki Koszalińskiej, Zeszyt Nr 21, Koszalin 2003.