# Effect of oxidant:feedstock ratio on the black coal oxidative desulphurization

Yuriy Prysiazhnyi, Serhiy Pyshyev, Volodymyr Gynka

Department of chemistry and technology of petroleum and gas, Institute of Chemistry and Chemical Technology, Lviv Polytechnic National University, UKRAINE, Lviv, S. Bandery street 12, E-mail: prysiazhnyi@ukr.net

Abstract – There are two interrelated factors in the process of coal oxidative desulphurization: time and oxidant consumption ratio. However, the total amount of air fed per feedstock unit has the key effect.

Key words - coal, oxidant, desulphurization, oxidant consumption, duration, sulphur (IV) oxide.

## I. Introduction

The black coal oxidative desulphurization takes place via treatment of high-sulphuric feedstock by the oxidant at the temperatures about 425 °C. Air-steam mixture with the optimum steam:air ratio of 30:70 (v/v) is used as an oxidant [1].

As a result of the process the pyritic sulphur (the main part of sulphur in the high-sulphuric coal) selectively converts into  $SO_2$ . The latter may be removed from desulphurization gases by known methods due to its high concentration in them (5-7 vol %). All these actions allow to reduce the sulphur (IV) oxide emissions into atmosphere while coal burning.

Process time and oxidant consumption ratio are the main factors affecting the process efficiency. It is known that these two factors are interrelated, namely the increase of one factor decreases the other value. Very often it is possible to change the quality of products obtained under different time and oxidant consumption but the same ratio between total amount of feedstock and oxidant [2].

Thus the aim of this work is to establish the relation between time and oxidation consumption ratio during the black coal oxidative desulphurization.

## II.Initial materials

To carry out the oxidative desulphurization we used black coal of the medium metamorphism degree (type G) withdrawn at "Lisova" mine of Lviv-Volyn basin.

The experiments were carried out using 0.1-0.25 mm fraction because such size of grains is the optimum one for the process [3, 4]. The analysis of the initial feedstock is represented in Table 1.

#### TABLE 1

CHARACTERISTICS OF THE INITIAL FEEDSTOCK

| W <sup>a</sup> , wt | A <sup>d</sup> ,<br>wt % | V <sup>daf</sup> ,<br>wt % | Sulphur content relative to the dry mass wt % |             |   |  |  |
|---------------------|--------------------------|----------------------------|---|-------------|---|--|--|
|                     |                          |                            | $S^{d}_{t}$                                   | $S^{d}_{p}$ | $S^{\scriptscriptstyle d}_{\scriptscriptstyle o}$ | $S^{\scriptscriptstyle d}_{\scriptscriptstyle SO_4}$ |  |
| 1.87                | 21.97                    | 36.71                      | 6.97  | 4.50        | 1.17  | 1.30   |  |

On the basis of the yield of desulphurized coal and sulphur content in it we calculated the conversion degree of pyritic sulphur, wt%:

$$\Delta S_{p}^{a} = \frac{S_{p0}^{a} \cdot 100 - S_{p}^{a} \cdot x_{c}}{S_{p0}^{a}}$$

where:  $s_{p0}^{a}$  - content of pyritic sulphur in the initial coal

relative to the analytic sample, wt %.;  $s_p^a$  - content of pyritic sulphur in the desulphurized coal relative to the analytic sample, wt %.;  $x_c$  - desulphurized coal yield, wt%.

## III. Investigation results

To determine the oxidant consumption ratio (OCR) under which it is advisable to carry out the desulphurization process varying the process time, we calculated minimum amount of the oxidant ( $m^3$  of air per kg of coal) consisted of oxygen minimum amount (and correspondingly air amount) necessary to oxidize pyrite (MAA<sub>1</sub>) and air minimum amount (MAA<sub>2</sub>) necessary to oxidize the coal organic matter (COM).

The minimum quantity of air necessary to oxidize all pyritic sulphur of the investigated coal is  $0.203 \text{ m}^3/\text{kg}$ . MAA<sub>1</sub> was determined taking into account FeS<sub>2</sub> conversion according to the following equation:

$$4\text{FeS}_2 + 11\text{O}_2 \rightarrow 2\text{Fe}_2\text{O}_3 + 8\text{SO}_2$$

 $MAA_2$  was calculated from the characteristics of desulphurization gases (volume and content of CO and CO<sub>2</sub> in them). MAA<sub>2</sub> is 0.238 m<sup>3</sup>/kg at the maximum temperature of 475 °C [1].

The total minimum amount of air necessary to carry out the pyrite and COM oxidation is 0.441 m<sup>3</sup>/kg. To ensure such ratio between air and coal at the average time of 15 min and steam content of 30 vol% [1] the minimum theoretical oxidant consumption ratio (MTOCR) should be 2.52 m<sup>3</sup>/(h·kg).

On the basis of all mentioned above the experiments were carried out at OCR value less than MTOCR (2.40  $m^3/(h\cdot kg)$ ) and thrice-repeated air excess (7.20  $m^3/(h\cdot kg)$ ).



168 "CHEMISTRY & CHEMICAL TECHNOLOGY 2013" (CCT-2013), 21–23 NOVEMBER 2013, LVIV, UKRAINE



in the desulphurization gases vs process time



The most intensive conversion of pyritic sulphur takes place during the first 5-15 min regardless of OCR (Fig. 1). The nature of  $SO_2$  concentration dependent on process time (Fig. 2) also confirms this fact. The maximum content of sulphur (IV) oxide in the desulphurization gases accounts for this time. The further increase of time increases gases volume and hence, the decrease of  $SO_2$ content in them.

While comparing the dependence of process efficiency on total consumptions of air and feedstock (air ratio, AR, m<sup>3</sup> of air per 1 kg of feedstock) we see the same values of pyritic sulphur conversion degrees and SO<sub>2</sub> concentration in the obtained gases (Figs. 3 and 4) at different values of OCR and time.Therefore, neither OCR nor time, but total amount of air per feedstock unit has the key effect on the desulphurization process. The calculation of the coefficient of air excess ( $K_{ae} = AR/MAA_1$ , Table 2) proves that total amount of air per feedstock unit should exceed its theoretical amount by 6.2-6.9 times to achieve the pyritic sulphur conversion degree 85-92 % at 425-450 °C and water steam content in the oxidant 30-50 vol %.



in the desulphurization gases vs air ratio

TABLE 2

DEPENDENCE OF PYRITIC SULPHUR CONVERSION DEGREE (PSCD) ON THE COEFFICIENT OF AIR EXCESS

| T, ℃ | X <sub>steam</sub> ,<br>vol %. | OCR,<br>m <sup>3</sup> /(h·kg) | τ,<br>min. | AR,<br>m <sup>3</sup> /kg | PSCD, % | K <sub>ae</sub> |
|------|--------------------------------|--------------------------------|------------|---------------------------|---------|-----------------|
| 425  | 0,3                            | 7,20                           | 15         | 1,26                      | 89,94   | 6,22            |
| 425  | 0,3                            | 2,40                           | 45         | 1,26                      | 85,29   | 6,21            |
| 425  | 0,3                            | 7,20                           | 15         | 1,26                      | 88,74   | 6,22            |
| 425  | 0,3                            | 4,81                           | 25         | 1,40                      | 91,75   | 6,91            |
| 445  | 0,5                            | 7,10                           | 21,5       | 1,27                      | 85,48   | 6,27            |

## Conclusions

The experimental results demonstrate the time and oxidant consumption ratio are interrelated factors of oxidative desulphurization. Neither OCR nor time, but total amount of air per feedstock unit has the key effect on the desulphurization process.

### References

- [1] S. Pyshyev, V. Gunka, Y. Prysiazhnyi, K. Shevchuk, A. Pattek-Janczyk, "Study of oxidative desulphurization process of coal with different metamorphism degrees", Journal of fuel chemistry and technology, vol. 40, no2, pp. 129-137, Feb. 2012.
- [2] R. B. Gyn, Neftyanuye bitymu [Petroleum bitumen]. Moskva: Himiya Publ., 1973.
- [3] S. V. Pyshyev, Oksudaciyna desylfyruzaciya vusokosirchustogo nyzkometamorfizovanogo vygillya [Oxidative desulphurization of high sulphur lowmetamorphized coal]. Lviv: Vydavnytstvo Lvivskoi politekhniky Publ., 1999.
- [4] H. V. Shevchyk, Oksudaciyne znesirchyvannay vysokometamorfizovanogo energetychnogo vygillya [Oxidative desulphurization of high-metamorphized energy coal]. Lviv: Vydavnytstvo Lvivskoi politekhniky Publ., 2009.

"CHEMISTRY & CHEMICAL TECHNOLOGY 2013" (CCT-2013), 21–23 NOVEMBER 2013, LVIV, UKRAINE 169