

HYDROGEN PRODUCTION BY TWO-STAGE CO-PYROLYSIS OF BITUMINOUS COAL-POLYMERS MIXTURES

Pavel STRAKA * and Vlastimil KRÍŽ

*Institute of Rock Structure and Mechanics, Academy of Sciences of the Czech Republic, v.v.i.,
V Holešovičkách 41, 182 09 Prague, Czech Republic*

**Corresponding author's e-mail: straka@irms.cas.cz*

(Received February 2008, accepted March 2008)

ABSTRACT

The two stage co-pyrolysis method for obtaining of hydrogen is described. In the course of the heating of the mixture of bituminous coal with polyisoprene and styrene-butadiene polymers (co-pyrolysis), a considerable amount of hydrogen and hydrocarbons is released in dependence on the process conditions. The experiments proved that the amount of hydrogen increased already with slightly increased heating rate (5 K min^{-1}) in comparison with the amount obtained at a common heating rate (3 K min^{-1}) and, further, with the addition of the second (cracking) stage for further thermal splitting of released hydrocarbons into hydrogen (and carbon), preferably at a temperature of $1200 \text{ }^\circ\text{C}$.

KEYWORDS: co-pyrolysis, coal, polymers, hydrogen

1. INTRODUCTION

For ecological reasons, hydrogen will become in the near future an important, clean fuel, but the question of its sources and the methods for obtaining it is still open. Great prospects for hydrogen formation can be provided by reactions taking place in the mixtures of bituminous coals with synthetic polymers while they are heated together (co-pyrolysis). But also another, quite different ways for production of hydrogen (and alkanes), e.g. aqueous-phase catalytic processes (Huber and Dumesic, 2006) are considered. In the overview is discussed how the aqueous-phase catalytic processes can be used to convert biomass into hydrogen and alkanes ranging from C_1 to C_{15} . Hydrogen can be produced by aqueous-phase reforming of the biomass-derived oxygenated hydrocarbons at low temperatures ($423\text{--}538 \text{ K}$) in a single reactor over supported metal catalysts. As till this time it is not clear which way is optimal the different possibilities must be considered and compared. In our case, co-pyrolysis of coal with unused polymers is discussed.

The formation of hydrogen is given by the behavior of the molecules of coal and polymers during thermal treatment and the related development of gases (Straka, 2003). Ability of coal to give molecular hydrogen arises from its chemical constitution. It was proved (Straka, 2002) that representative structures of bituminous coals are the clusters with 2–4 aromatic rings and 1–2 OH groups, and side cycles formed mainly from six-membered cyclanes with methyl groups or six-membered heterocyclanes with aliphatic substituents. The clusters are joined together by the

methylene- or ethylene bridges, or by oxygen ones. As hydrocarbons structures represent quantitatively main component of coal substance, coal releases a considerable amount of molecular hydrogen during its thermal decomposition. This amount can be further increased by addition of suitable polymer containing more hydrogen than coal. For instance, if hydrogen content in coal substance is 4.77 wt.-% and that in the polymers mixture 7.87 wt.-%, then more hydrogen will be recovered from coal in the polymers mixture presence.

During thermal splitting of coal structures, hydrogen is released chiefly from alicyclic rings and methylene bridges. The energy of the splitting of alicyclic rings ($289\text{--}368 \text{ kJ mol}^{-1}$, on average 341 kJ mol^{-1} (Buryan and Macák, 1977)) is comparable e.g. with the energy of the splitting of etheric bonds, so thermal decomposition of coal structures takes place relatively easily, the result of which is the development of hydrogen and hydrocarbons. For instance, ethane develops in the range of $285\text{--}640 \text{ }^\circ\text{C}$ (the maximum at $400 \text{ }^\circ\text{C}$), ethene in the range of $280\text{--}600 \text{ }^\circ\text{C}$ (the maximum at $410 \text{ }^\circ\text{C}$), propan in the range of $275\text{--}615 \text{ }^\circ\text{C}$ (the maximum at $415 \text{ }^\circ\text{C}$) and propene in the range of $370\text{--}610 \text{ }^\circ\text{C}$ (the maximum at $420 \text{ }^\circ\text{C}$). That means that already the softening of the coal substance is preceded and accompanied by the splitting of alicyclic rings and methylene bridges while hydrogen and hydrocarbons are being released, the latter of which are capable of providing additional hydrogen through further thermal splitting. Thus, formation of hydrogen and hydrocarbons during pyrolysis is connected with a

plastic state of coal which generally occurs in the temperature range of 350–550 °C.

According to thermal measurements (Blažek, 2005) and thermal behavior data (Braun, 1999; Mleziva, 1983), the decomposition of synthetic polymers falls often in the temperature rank of plastic state of coal. In our case, a model mixture of polyisoprene with styrene-butadiene copolymer was used. The thermal decomposition of this polymers mixture occurs in the temperature range of 320–500 °C, intensively at 390–440 °C; its hydrogen content is significantly higher than in coal used (7.87 wt.-%, in contrast to coal – 4.77 wt.-% (daf)). It means that addition of considered admixture of polymers to coal can lead to increase of amount of hydrogen released during heating of the charge (co-pyrolysis). As hydrocarbons are also formed during heating of the mixture in question, the addition of the second, cracking stage for their thermal splitting into hydrogen and carbon can further increase the hydrogen yield. On the whole, a two-stage co-pyrolysis is a promising way of obtaining hydrogen.

Besides its chemical constitution, bituminous coal has prerequisites to become an important source of hydrogen also in terms of occurrence and lifetime of reserves. This is based on an estimate of geological reserves of coal ($15 \cdot 10^{12}$ tons) with the lifetime of coal reserves being more than 200 years and on the fact that on the worldwide scale bituminous coal mining significantly predominates over brown coal mining. Another source can be biomass (Minowa et al., 2004), but also unused synthetic polymers (Kříž and Brožová, 2007), which, as has been shown by experiments so far, yield substantial amounts of hydrogen when heated in a mixture with coal. Important methods for obtaining hydrogen will thus be derived from pyrolysis of coal, or from co-pyrolysis of coal with above-mentioned admixtures. Since, apart from other gases, beside hydrogen different hydrocarbons will be obtained through a simple pyrolysis/co-pyrolysis in one stage, it is necessary to employ a two-stage pyrolysis/co-pyrolysis so that the splitting of these hydrocarbons into hydrogen (and carbon) could occur.

As was mentioned above, the formation of hydrogen and hydrocarbons, but also other gases, during pyrolysis of bituminous coal is connected with a plastic state. In the case of coals from the Czech Part of the Upper Silesian Basin (our case), the beginning

of the plastic state (coal softening temperature) was found at 415 \pm 7 °C, maximum fluidity at 450 \pm 8 °C and finally the end of the plastic state (temperature of re-solidification of coal structure) at 481 \pm 8 °C (Straka, 2003). (These data were obtained by measuring of 95 samples of the bituminous coals in question, differing petrologically, by coal type, elemental composition, proximate analysis parameters and coking properties.) The maximum fluidity of coal in the plastic state was ascertained to be in the wide range of 15–1920 ddp_m and cumulative fluidity in the range of 107–12062 ddmp, but all the samples had almost the same softening, maximum-fluidity and re-solidification temperatures. The course of the development of the gases, which in the case of the individual coals was quite similar, also corresponded to the practically constant temperature characteristics of the plastic state. On the whole, the temperature range of the plastic state of coals from the Czech Part of the Upper Silesian Basin can be realistically considered to be in the range of approximately 410–480 °C. In this range, hydrogen, methane, ethene and ethane, propene and propane, C₄ hydrocarbons, carbon monoxide and carbon dioxide, nitrogen and ammonia and hydrogen sulfide are intensively released through the splitting of coal molecules. Methane and hydrogen, however, are released not only in the plastic state, like the other above-mentioned gases, but in a wide range, from about 300 up to 1000°C. This makes them different from other gases and makes coal an important source of hydrogen, because the CH₄ molecule is further splittable into H₂ and elemental carbon.

The aim of the presented work is to describe the influence which the conditions of a two-stage co-pyrolysis (mainly heating rate, the final temperature of the first stage, polymers addition and the temperature of the second stage of heating) have on the amount of the hydrogen obtained.

2. EXPERIMENTAL

Low-ash (3 wt.-%, dry basis) and low-sulfur (0.4 wt.-% total sulfur, dry basis) bituminous coal (swelling index=1, VM=30.8 wt.-%) from the Czech Part of the Upper Silesian Basin (the Lazy Mine) (Table 1) was used for the experiments and was the base of the charges put into the reactor. The model mixture containing polyisoprene, styrene-butadiene copolymer, ash matters and the small amounts of nitrogen- and sulfur organic compounds (Mleziva,

Table 1 Proximate and ultimate analysis of the used Lazy coal (wt.-%). O_d – oxygen calculated by difference.

Proximate analysis			Ultimate analysis				
Water	Ash (dry basis)	S _t ^d	C	H	N	S _o	O _d
0.9	3.21	0.37	84.17	4.77	1.18	0.35	9.53

Table 2 Proximate and ultimate analysis of the used polymers admixture (wt.-%). O_d – oxygen calculated by difference.

Proximate analysis			Ultimate analysis				
Water	Ash (dry basis)	S _t ^d	C	H	N	S _o	O _d
1.20	5.11	1.30	87.70	7.87	0.62	1.37	2.44

Table 3 List of experiments. Ps – polymers admixture.

Experiment No.	Charge	Process	Temperature of the 2 nd stage (°C)
1	Coal	One-stage pyrolysis	-
2	Coal	Two-stage pyrolysis	1000
3	Coal	Two-stage pyrolysis	1100
4	Coal	Two-stage pyrolysis	1200
5	Coal + 15 % Ps	One-stage co-pyrolysis	-
6	Coal + 15 % Ps	Two-stage co-pyrolysis	1100
7	Coal + 15 % Ps	Two-stage co-pyrolysis	1200

Table 4 Mass balances of one-stage pyrolysis and co-pyrolysis (wt.-%) (dry charge=100 %).

Experiment No.	Coke	Tar	Water	Gas	Losses
1	73.4	8.0	5.9	11.1	1.6
5	68.5	15.4	5.5	8.6	2.0

1983) was used as an admixture (VM=68.9 wt.-%) (Table 2). The content of this polymers admixture in the charges was 15 wt.-% each time. The bulk density of the used Lazy coal alone was 769 kg m⁻³ while of the coal with 15 wt.-% of polymers admixture was 667 kg m⁻³.

Charges with a weight of 100 g were pyrolyzed/co-pyrolyzed in a vertical quartz reactor placed in an electric resistance furnace until the final temperature of 900 °C (the first stage), and the products of the thermal decomposition (tar and reaction water) were further led and split in a horizontal cracking reactor at the temperatures of 1000, 1100 and 1200 °C (the second stage). This cracking reactor was closely connected with the outlet of the reactor of the first stage.

For the steady formation of the volatile products, the following temperature regime for the heating of the charges was empirically found and applied in the first stage. In the interval 25–450 °C (drying, plastic state and development of gases), the heating took place at a rate of 5 K min⁻¹; then from 450 to 650 °C (intensive tar formation at 450–550 °C, formation of semi-coke, intensive development of gases) at a slightly reduced heating rate under 5 K min⁻¹, and from 650 °C to the final temperature of 900 °C

(formation of the final solid carbonaceous residue/coke, further development of hydrogen and methane) again at a rate of 5 K min⁻¹. The soaking time at the final temperature was 30 min (the maturation of the solid residue, further development of hydrogen). This first-stage process was considered as the one-stage pyrolysis/co-pyrolysis at 5 K min⁻¹ because prevailing heating rate was 5 K min⁻¹. The slightly reduced heating rate was used only for rather slower development of volatile products in the above-mentioned temperature range without any influence on yield of tar and gas.

The formed raw gas from the first stage was immediately led into the horizontal flow quartz reactor working at temperatures of 1000, 1100 and 1200 °C (the second stage), which was closely linked to the outlet of the reactor of the first stage. In this horizontal flow quartz reactor the cracking to the final hydrogen-rich gas and amorphous and structured carbon took place. This additional cracking together with one-stage pyrolysis/co-pyrolysis was considered as two-stage process. List of experiments is in Table 3. The mass balances of the one-stage pyrolysis of coal and co-pyrolysis of coal with polymers are stated in Table 4.

Table 5 Composition of the gas mixtures from pyrolyses and co-pyrolyses (vol.-%). N₂(r) – nitrogen formed during the thermal decomposition.

Experiment No.	H ₂	CH ₄	C ₂ H ₄	C ₂ H ₆	C ₃ H ₆	C ₃ H ₈	ΣC ₄	N ₂ (r)	CO	CO ₂
1.	59.31	24.13	0.35	1.78	0.25	0.40	0.12	2.05	7.76	3.85
2.	63.96	19.66	0.41	1.85	0.25	0.33	0.09	2.05	8.79	2.61
3.	71.77	14.56	0.26	0.04	0.00	0.02	0.00	1.32	10.41	1.62
4.	77.36	5.43	0.04	0.00	0.00	0.00	0.00	1.73	14.40	1.04
5.	61.18	24.04	0.46	2.04	0.26	0.54	0.11	1.91	6.23	3.23
6.	74.40	13.64	0.18	0.03	0.00	0.01	0.00	1.87	9.02	0.85
7.	80.60	3.75	0.03	0.00	0.00	0.00	0.00	1.58	13.66	0.38

The resulting gas was collected in a gas-holder and analyzed both continuously and as a whole. For the continuous analysis of hydrogen, a Teledyne's Series 2230 GP Pd/Ni Analyzer was used; CH₄, CO, CO₂ were analyzed in the same way with Teledyne's Series 7500 Infrared Gas Analyzer. The gaseous components of the total gas were determined on gas chromatographs Agilent Technologies 6890N System with FID and TCD detectors. Properties of the gas mixtures were calculated according to the ČSN 38 5509 standard (Technical gas constants).

3. RESULTS AND DISCUSSION

The experiments were conceived in such a way as to clarify both the influence of the temperature conditions of pyrolysis (heating rate, final temperature and soaking time) and the influence of the admixed polymers on the amount of the hydrogen obtained. It was also important to determine the temperature for the second stage of the decomposition of tar or hydrocarbon components in raw gas which is decisive for the intensity of their secondary decomposition into hydrogen and elemental carbon and contributes to a considerable increase of the hydrogen content in the final gaseous mixture.

Pyrolysis experiments proved that the coal alone, heated in a single stage at a standard rate (used for coke production and standard pyrolyses (Roubíček and Buchtele, 2002) of 3 K min⁻¹ to the final temperature of 900 °C yielded pyrolysis gas with a content of 54 % H₂ and 22 % CH₄. No significant increase of hydrogen content with increasing of final temperature to 1000°C or prolongation of the soaking time to 60 min was observed. On contrary, the increase of the heating rate to 5 K min⁻¹ brought an increase of H₂ content to 59 % and CH₄ to 24 %. Therefore, for the sake of comparison, the coal alone and coal with 15 % of polymers were first pyrolyzed and co-pyrolyzed in a single stage with the heating rate being increased to 5 K min⁻¹ (one-stage process). The amounts of the hydrogen and methane obtained were subsequently compared with the amounts obtained by two-stage process at the temperatures in

the second stage: 1000, 1100 and 1200 °C. The results are summarized in Table 5.

It is evident that even a small increase of the heating rate supports the splitting of alicyclic rings and aliphatic groups in coal structure, and besides a considerable increase in the amount of hydrogen also brings the possibility of its additional formation through the secondary splitting of an increased amount of methane in the second stage. With the addition of the second stage at a temperature of 1000 °C, only a small increase of H₂ vol. % to 64 was achieved in the resulting gas while the CH₄ content fell to 20 % (Table 5), but at 1100 °C the hydrogen content was already 72 % with the CH₄ content being reduced to 15 %. However, since a further increase of the temperature in the second stage to 1200 °C did not bring the expected increase of the hydrogen content in the total gas any more (only to 77 % H₂), the composition of the charge was altered by the addition of 15 wt.-% of polyisoprene–styrene–butadiene admixture, whose carbon content was similar to this in coal (Tables 1 and 2) and which contained aliphatic, easily splittable structures (volatile matters=68.9 wt.-%). Moreover, as was stated above, its hydrogen content was significantly higher and oxygen lower than in coal.

The charges with 15 % of the mentioned polymers heated in a single stage at a rate of 5 K min⁻¹ yielded pyrolysis gas with the content of 61 % H₂ and 24 % CH₄. It was therefore expedient also in this case to add the second stage of co-pyrolysis, because the methane content was rather high. As it arose from the preceding experiments, the splitting of hydrocarbons in the second stage at a temperature of 1000°C manifested itself in the resulting gas by only a small increase of H₂ content, the two-stage co-pyrolysis was conducted at temperatures of 1100 and 1200 °C in the second stage. At the temperature 1100 °C, 74 % H₂ with 14 % CH₄ were obtained. These amounts were practically almost the same as in the case of the two-stage pyrolyses of coal alone, and therefore the temperature of the second stage was increased to 1200 °C. This

Table 6 Properties of the gas mixtures from pyrolyses and co-pyrolyses. V_N – normalized volume of gas obtained from 100 g of charge, Q_s – gross calorific value, s – gas density, m_g – yield of gas (dry charge=100 %).

Experiment No.	1	5	2	3	6	4	7
H ₂ (vol.-%)	59.31	61.18	63.96	71.77	74.40	77.36	80.60
V_N (dm ³)	23.7	19.3	28.0	36.3	40.7	44.4	51.5
Q_s (MJ/m ³)	20.45	20.85	19.36	16.50	16.22	13.89	13.53
s (kg/m ³)	0.469	0.445	0.429	0.335	0.320	0.331	0.297
m_g (wt.-%)	11.1	8.6	12.0	12.1	13.0	14.7	15.3

increase in the hydrocarbons splitting temperature already brought a considerable increase in the amount of the hydrogen released with a significant reduction in the amount of methane, because 81 % H₂ and only 4 % CH₄ were found in the total gas. Gas containing 81 % hydrogen can already be considered as hydrogen-rich, with conditions for its acquisition being acceptable also on an industrial scale: the co-pyrolyzed mixture had a bulk density of 667 kg m⁻³, the heating rate was 5 K min⁻¹, the temperatures 900 °C and 1200 °C, with the content of the admixed polymers being 15 %. It is vital that this proportion can be further increased, which would probably yield more hydrogen.

The total gas contained low amounts of CO₂ but quite high amounts of CO (Table 5). This is without doubt a favorable feature of the method of co-pyrolysis applied, because CO positively contributes to the energy content of the obtained gas and to its yield. The differences are significant mainly in the cases of two-stage co-pyrolyses, when CO₂ was reduced to CO by action of formed elemental carbon during cracking process in the second stage. Properties of the gas mixtures calculated according to above-mentioned technical gas constants standard and based on results obtained both from pyrolyses and co-pyrolyses are summarized in Table 6. From the data in Table 6 it follows that with an increasing of hydrogen content the normalized volume and the yield of gas obtained increase, on contrary, gas density and gross calorific value (Q_s) decrease. These results show that the trends of key parameters – Q_s and the yield of hydrogen-rich gas – are opposed: if the yield increases, the Q_s decreases. It means that, if necessary, decreasing of the Q_s could be compensated by increasing of the hydrogen-rich copolymer/polymer content in the mixture. Further, it arises from the data acquired that the two-stage co-pyrolysis gas could be a realistic source of hydrogen. For comparison, another method being considered now can be well-known coal gasification by steam in the presence of lime (through which CO₂ is eliminated in situ), adapted to waste polymer mixtures use. The gasification has to be performed under high pressure (10 MPa) so that the high-end temperature of

gasification could be below 650 °C. Otherwise, reverse decomposition of the formed CaCO₃ to CO₂ would occur without its being removed. The driving reaction of the process is the combination of CaO with CO₂ during the gasification, which is an exothermic reaction producing heat for coal gasification reactions. High-temperature CO₂ capture shifts the reaction balance of key reactions in favor of hydrogen. When we compare the two methods, a significant drawback of gasification is that it uses lime, which has to be made from limestone with high energy consumption and carbon dioxide emissions. Also the price of limestone is rather high now, because it is used for desulphurization during fluid combustion. An increase of the amount of hydrogen through polymer or copolymer addition has not been successfully proven in the case of this method. Consequently, the results for a two-stage co-pyrolysis seem better from this comparison, because it does not require any other admixture than the waste synthetic polymers, which would otherwise end up in a landfill.

4. CONCLUSIONS

It was established that already a small increase of heating rate (from 3 to 5 K min⁻¹), a reasonable polymers addition (15 %) and a suitable temperature for the secondary hydrocarbon decomposition (1200 °C) will increase the hydrogen content in the obtained total gas by 20 vol.-%. Since the hydrogen content is then over 80 vol.-%, we can talk about a hydrogen-rich gas, which can already be used for ecological combustion and having been further purified also for fuel cells. Another increase of H₂ content can probably be reached by increasing the polymers content in the mixture. A two-stage co-pyrolysis is thus likely to be a promising method for obtaining hydrogen.

ACKNOWLEDGEMENT

This work was supported by the Czech Science Foundation (GA ČR) as the project no. 105/07/1407.

REFERENCES

Blažek, J.: 2005, Study of the reaction kinetics of the thermal degradation of polymers. PhD Thesis, Institut

- National Polytechnique de Toulouse and Institute of Chemical Technology, Prague.
- Braun, D.: 1999, Simple methods for identification of plastics. Fourth Edition, Hanser Publisher, Munich 1999.
- Buryan, P. and Macák J.: 1977, Fenols in coal pyrolysis products II, *Chemické Listy* 71, 829- 837, (In Czech).
- Huber, G.W. and Dumesic, J.A.: 2006, An overview of aqueous-phase catalytic processes for production of hydrogen and alkanes in a biorefinery, *Catalysis Today* 111, Issues 1-2, 119-132.
- Kříž, V. and Brožová, Z.: 2007, Co-pyrolysis of coal/waste polymers mixtures, *Acta Geodynamica et Geomaterialia*, Vol. 4, No. 2(146), 39-42.
- Minowa, T. et al.: 2004, Application of in-situ CO₂ removal gasification of woody biomass for hydrogen production. In: Proceedings of the 21st Annual Int. Pittsburgh Coal Conference, September 13-17, Session 15, Paper 15-2, Osaka.
- Mleziva, J.: 1983, Polymers – production, properties and usage. Sobotáles. Praha, (in Czech).
- Roubíček, V. and Buchtele, J.: 2002, Coal – sources, processes, usage. Montanex, Ostrava, (in Czech).
- Straka, P.: 2002, Solid-state NMR spectroscopy of Ostrava-Karviná coals, *Chemical Papers* 56(3), 182-187.
- Straka, P.: 2003, Chemical structure of coal substance, *Acta Montana*, Series AB, No. 12(132), 7-47.