

The promoting action of sodium carbonate should, therefore, be connected with the acceleration of the slowest stage which, in turn, determines the overall rate of reaction.

Owing to the application of gasification catalysts, one may be able to carry out the process at lower temperatures without reducing the reaction rate. This possibility may acquire a particular significance if a coal gasification unit is operated in association with a helium-cooled high-temperature nuclear reactor (HTR) [13]. In this method the gasification process with steam would occur in a fluidized bed of coal. The reaction heat from an HTR is passed on through a tube heat-exchanger located in the gas generator. This manner of heat transfer lowers the temperature of the gasification process in relation to the temperature of helium leaving the HTR. For example, when helium leaves an HTR at 900°C , coal gasification will take place at about 760°C ; at 1100°C , the gasification will be carried out at 800°C [13]. Thus, a 200°C rise in the helium temperature brings about only a 40°C increase in the temperature of gasification. The gasification temperatures, obtained by means of the heat from an HTR, are normally insufficient for high rates of reaction. Since the possibilities of raising the temperature of helium from an HTR, and thus, increasing the gasification temperature are so limited, it would be advantageous to raise the rate of the gasification reaction by the application of catalysts.

The present paper reports the results of studies on the effect of the amount of sodium carbonate added to char from a coal previously carbonized at $580\text{--}620^{\circ}\text{C}$, on the course of gasification with steam at $700\text{--}950^{\circ}\text{C}$ and atmospheric pressure. The low-temperature coal carbonization was carried out in order to obtain liquid products (tar) for further processing by hydrogenation, and thus, to produce liquid fuels. In an attempt to achieve complex coal processing, it seems purposeful and advantageous to convert the low-temperature coke, remaining after coal carbonization, into gaseous fuels or hydrogen, needed in large quantities for tar hydrogenation.

Methods

Experiments were carried out on low-temperature char obtained from coal by the fluidized-bed method [14] in the Institute of Chemical Coal Processing in Zabrze (Poland). The coal used was of non-coking type and was characterized by large yields of volatile matter. The analysis of the char is shown in Table 1. The char was impregnated with a solution of sodium carbonate

Table 1. Analysis of char from low-temperature carbonization

Proximate analysis (wt % , air - dried basis)	
Moisture	0.2
Volatile matter	16.2
Fixed carbon	72.4
Ash	11.2
Ultimate analysis (wt % , dry, ash - free basis)	
C	82.4
H	4.0

or sodium hydroxide, introducing Na_2CO_3 in quantities of 5 wt % (2.9 % of Na_2O) up to 40 wt % (23.6 % of Na_2O), or NaOH in the quantity of 15.24 wt % (11.8 % of Na_2O). The particle size of the char used in the experiments ranged from 1.02 to 0.5 mm.

The gasification rate of the char was determined gravimetrically using an analytical balance connected to a quartz flow reactor, 38 mm i.d. A dry sample of coke (about 0.23 g) was spread as a thin layer on a flat quartz scale (22 mm in diameter) hanging on the balance arm. The reactor was heated by a stream of dried oxygen-free nitrogen (purified previously by passing through the catalysts: Cu SiO_2 at 200°C and Ni on $\gamma\text{-Al}_2\text{O}_3$ at 420°C at a flow rate of 1.5 l/min., up to the temperature of measurement, then the nitrogen was saturated with steam. The mixture of nitrogen and steam contained 30 mol. % of steam (the steam partial pressure was 300 hPa). The change in the mass of the char during gasification determined the percentage of coal gasification ($\Delta m/m \cdot 100$, where m - mass of char at reaction temperature, Δm - loss of mass after time t)

and the gasification rate ($-dm/m : dt$). After the reaction of 25 % and 50 % of the coal, the gasification rate was determined graphically from the plot of $\Delta m/m \cdot 100 = f(t)$.

The effect of sodium carbonate addition on the gas composition from gasification of low-temperature char was examined in a steel flow-reactor (38 mm i.d.) with a fixed coal bed (height about 10 cm). After heating the coke to the reaction temperature in a nitrogen stream, the flow of nitrogen was cut off and water (19 ml/h) was passed into a vaporizer by a water feed pump. The steam produced was passed on to the reactor. The product gas was then dried and its composition was determined by gas chromatography.

RESULTS

The effect of the amount of sodium carbonate on the gasification rate is shown in Fig. 1. The results confirm and complete the data available in the literature. Addition of sodium carbonate to char before gasification with steam and the increase in reaction temperature both raised the reaction rate. The introduction of 20 wt % sodium carbonate increased the gasification rate quite distinctly. A further increase in the amount of catalyst brought about a smaller increase in gasification rate - particularly well seen at lower temperatures of reaction. These interdependencies were observed both at 25 % and 50 % of reacted coal, although in the latter case the gasification rates were considerably smaller. The addition of 20 wt % of sodium carbonate, at 25 % of reacted coal and at 750°C, made it possible to achieve a gasification rate equal to that of catalyst-free char gasification at 950°C. With 50 % of reacted coal the same amount of sodium carbonate made it possible to reach at 750°C the same gasification rate as that of untreated char at 920-930°C. At the same time, with 20 wt % of sodium carbonate, at 750°C one may reach a gasification rate over ten times as high as that without a catalyst.

The introduction of sodium carbonate also produced a gas of different quantitative composition. Figure 2 presents the contents of the main components in the dried product gas, i.e.

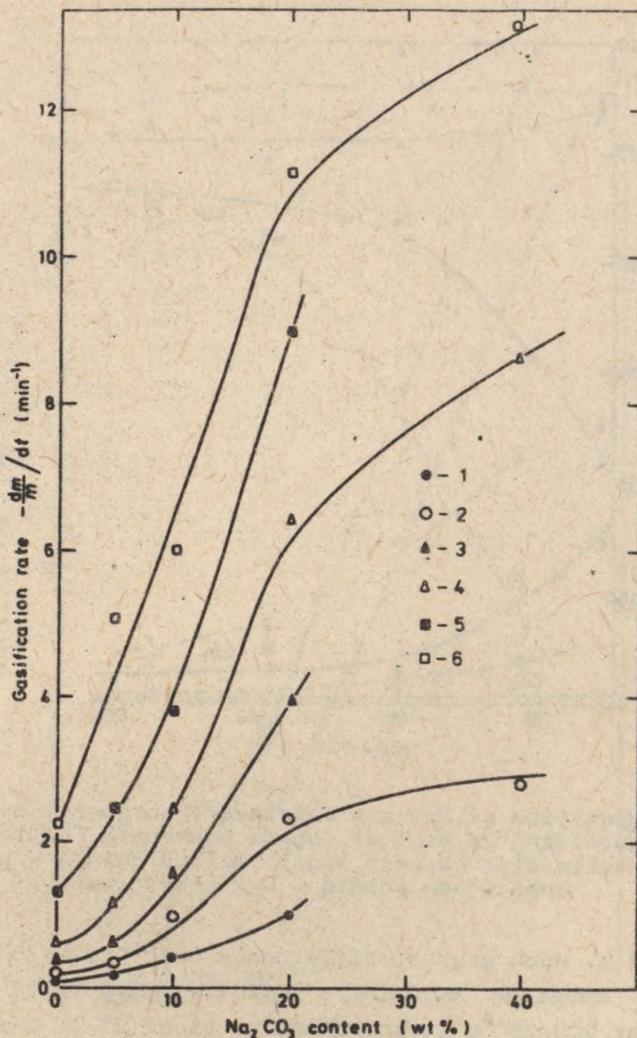


Fig. 1. Effect of sodium carbonate on gasification rate of the char (with 25 % of char reacted); reaction temperature: 1 - 700°C, 2 - 750°C, 3 - 800°C, 4 - 850°C, 5 - 900°C, 6 - 950°C

hydrogen, carbon monoxide, carbon dioxide, and methane, obtained from the gasification of untreated char and of char impregnated with sodium carbonate. In both cases, the obtained gas contained mostly hydrogen (about 50-55 %). The hydrogen content slightly decreased with the reaction temperature. An addition of sodium carbonate reduced the amount of hydrogen obtained

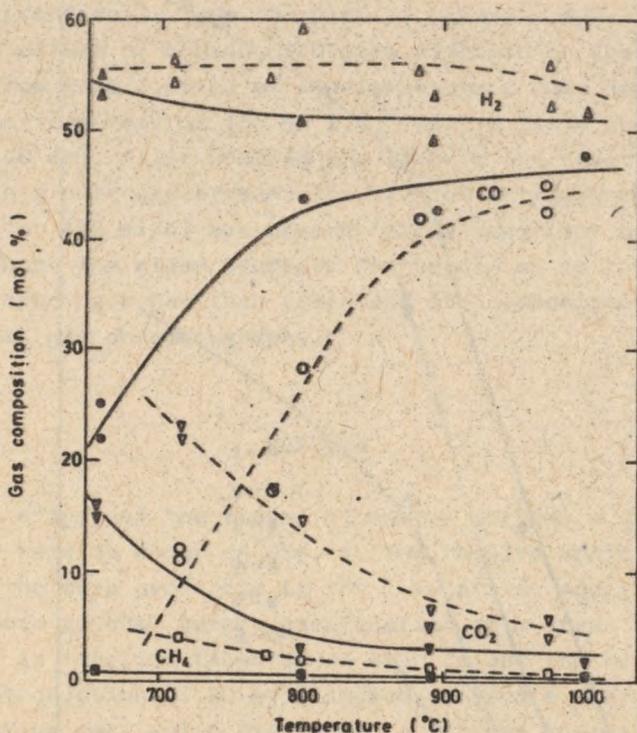


Fig. 2. Composition of dry gas obtained from gasification of the char containing 20 wt % of sodium carbonate (solid line) and of untreated char (broken line); filled points - treated char; open points - untreated char

by only 2-5 %. Much greater differences occurred in the amounts of carbon monoxide produced - with the addition of sodium carbonate at 700-750°C it increased by about 20 %, though at higher temperatures this difference fell to a few per cent. At temperatures above 800°C the amounts of hydrogen and carbon monoxide produced were very similar. With increased carbon monoxide, the amount of carbon dioxide produced decreased. As with carbon monoxide, the greatest differences occurred at lower temperatures. The application of sodium carbonate also decreased the amount of methane produced, the more so, the lower the reaction temperature.

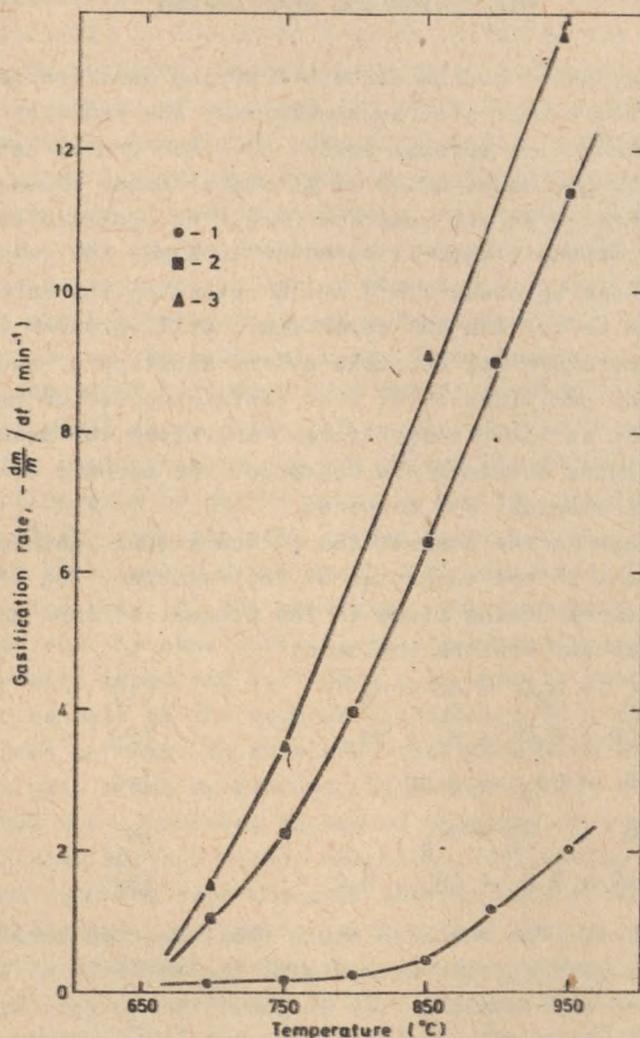


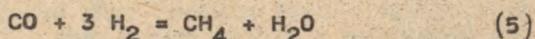
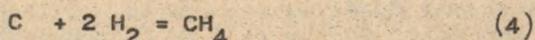
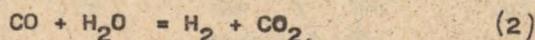
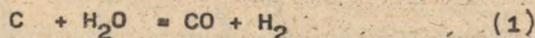
Fig. 3. Gasification rate of the char containing 11.8 wt % of Na_2O as Na_2CO_3 or NaOH (with 25 wt % of char reacted): 1 - char, 2 - char + Na_2CO_3 , 3 - char + NaOH

The comparison of the effects of the type of chemical compound containing sodium on the gasification rate of low-temperature char showed that sodium hydroxide acted more effectively than sodium carbonate. After the addition to char of the same amount of sodium, 11.8 wt % of Na_2O , in the forms of carbonate or hydroxide respectively, the latter increased more the rate of gasification than the former.

DISCUSSION AND CONCLUSIONS

The addition of sodium carbonate during gasification of the low-temperature char greatly accelerates the reaction of carbon with steam. The optimal amount of added sodium carbonate was quite large, about 20-25 wt %. Higher doses produced much smaller increase in the reaction rate. The addition of 20 wt % of sodium carbonate made it possible to lower the temperature of the process by about 200°C while retaining the same gasification rate as for the untreated char. Still greater lowering of the temperature was possible by the addition of sodium hydroxide. The gasification of char containing sodium carbonate, particularly at lower temperatures, increased the amount of carbon monoxide obtained and decreased the amounts of hydrogen, carbon dioxide, and methane.

The change in the composition of the product gas indicates modifications in the mechanism of the reaction. The main chemical reactions taking place in the process of coal gasification with steam, are the following:



It is known from the literature that, besides accelerating the rate of gasification with steam, the addition of sodium carbonate to char makes a rise in gasification rate with carbon dioxide [2,15,16], and with hydrogen [17], and in its combustion with oxygen [2,15,16]. It is also known that the reaction of carbon with steam is inhibited by hydrogen [18-21] while those of carbon with carbon dioxide and oxygen are inhibited by carbon monoxide [19,20,22-24]. The inhibitory action of hydrogen and carbon monoxide is usually accounted for by their strong adsorption or ability to react with surface oxide, accompanied by the production of water or carbon dioxide [19].

The results obtained by us imply a smaller participation of reaction (2) in the whole process, although the absolute rate of the reaction, according to ref. 3, may be higher. The participation of reaction (4) under the atmospheric pressure, plays a very slight part in the total process. The smaller amount of methane produced in the gasification of char in the presence of sodium carbonate, may result from a decrease in the rate of the methanation reaction (5) [25]. The increase in the content of carbon monoxide observed in the product gas might have been caused by a greater participation of reaction (3) in the whole process. Such changes in the course of reaction might be caused by a weaker binding of carbon monoxide produced in reaction (1) on the coal surface, and by its faster desorption to the gas phase. The sites on the coal surface liberated by carbon monoxide may be immediately occupied by water, reacting with carbon according to reaction (1), which, in turn, would bring about a considerable rise in the gasification rate. At the same time, the desorption of carbon monoxide from the coal surface makes impossible its further reaction with steam and hydrogen, according to reactions (2) and (5), as well as the reverse of reaction (1), taking place on the coal surface. In this way, the inhibition of coke gasification with steam by hydrogen is weakened. This statement implies that the inhibitory action of hydrogen is caused by its reaction with surface carbon monoxide. Facilitated desorption of carbon monoxide from the char surface also produces an acceleration of coal gasification with carbon dioxide and oxygen, and in both reactions carbon monoxide is produced. The introduction of sodium carbonate to char during gasification also causes a decrease in the acidity of the surface; the action of sodium hydroxide is still more effective. All those changes may lead to a great increase in chemisorption of steam and the increase in its concentration on the coal surface. Thus, the facilitation of water chemisorption and carbon monoxide desorption will increase the gasification rate and change the composition of the product gas.

We also believe that the rate of char gasification with steam is the highest at the site of contact between solid (or liquid - at temperatures higher than the melting point) sodium

carbonate with the char surface. The action of the catalyst at greater distances seems unlikely, and the rate of the reaction on the char surface far the char - sodium carbonate boundary probably does not change. The increase in reaction rate at boundary in relation to that on the remaining coal surface will produce channels that will deepen during the course of the reaction (Fig. 4).

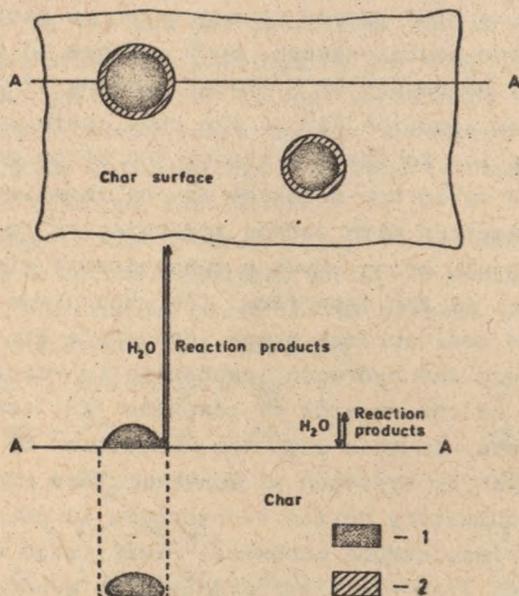


Fig. 4. Model diagram of catalytic action of sodium carbonate; 1 - catalyst, 2 - site of highest reaction rate, length of arrows corresponds to gasification rate

Such a phenomenon was observed during the hydrogenation and combustion of graphite in the presence of various catalysts [26-30]. An increase in the reaction rate on the boundary also makes it possible to explain the existence of an optimal amount of the catalyst. The initial increase in the amount of sodium carbonate on char brings about an additive increase in the length of the boundary, and, hence, a speedy rise in the reaction rate. With larger amounts, the covering of the char surface by sodium carbonate (and, thus, a decrease in the char

surface available to steam) begins to predominate over the increase in the length of the boundary, which is reflected in a smaller enhancement of gasification rate than with smaller amounts of sodium carbonate.

Considering the possibilities of applying sodium carbonate or hydroxide, as catalysts for coke gasification with steam, one should not forget the possibility of their escape from char during reactions taking place at higher temperatures, as well as their corrosive effect on the reactor. From the economic point of view, it is also important to know the possibilities for recovering and re-using sodium carbonate. The optimal amount of sodium carbonate constitutes a fairly large percentage of the char gasified. With the processing of many tons of coal, the recovery of sodium carbonate will determine the possibility of its application as a catalyst. It was shown in ref. 5 that it is possible to recover about 75 % of the carbonate used by washing the ash with hot water. Such methods are being worked out in studies on coal gasification by the Kellogg Process.

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STRESZCZENIE

Przedstawiono wpływ ilości węglanu sodowego, dodawanego do koksiku, na szybkość zgazowania w temp. 700-950°C pod ciśnieniem atmosferycznym. Optymalna ilość węglanu sodowego wynosi ok. 20-25 % wag. Taka ilość węglanu sodowego pozwala na obniżenie temperatury procesu o ok. 200°C przy nie zmienionej szybkości reakcji. Bardziej efektywnie działa wodorotlenek sodowy. Stosowanie węglanu sodowego jako katalizatora procesu powoduje wzrost ilości otrzymywanego tlenku węgla i zmniejszenie ilości dwutlenku węgla, wodoru i metanu. Przedyskutowano zmiany w mechanizmie reakcji, spowodowane obecnością katalizatora na powierzchni węgla.

Резюме

В данной работе представлено влияние количества карбоната натрия, добавляемого к коксину, на скорость газификаций при температурах 700⁰-950⁰С под атмосферическим давлением. Оптимальное количество карбоната натрия равняется около 20-25% веса. Такое количество карбоната натрия способствует понижению температуры процесса примерно на 200⁰С при неизменной скорости реакции. Более эффективно действует гидроокись натрия. Применение карбоната натрия как катализатора процесса вызывает повышение количества получаемого окиси углерода и снижение количества двуокиси углерода, водорода и метана. Рассмотрено изменения механизма реакции, вызванной наличием катализатора на поверхности угля.