International Gas Union Research Conference 2011

PARTIAL OXIDATION OF NATURAL GAS TO PRODUCE A CARBURIZING ATMOSPHERE FOR SURFACE TREATMENT OF STEEL

J. de Azevedo

BRAZIL

ABSTRACT

Conventional methods for surface treatment of metals, such as carburizing, rely on processing under high temperature in carbon rich atmospheres. The atmosphere is industrially generated using the partial oxidation of a carbon rich fuel, such as propane, butane and methanol. While methanol has been extensively used, with good results, it is relatively expensive and presents a hazard due to its toxicity. Natural gas is a promising alternative for conventional systems based on methanol because of its high availability in industry, relative low cost and ease of supply and distribution. However, methane rich natural gas (above 90% methane) is known to be a non-sooting gas, resulting in a relatively higher difficulty for decomposition in a free flame to carbon rich products in the required concentrations. Since the quality of the atmosphere, measured by its carbon potential, has a strong effect on the surface quality of the product, the production of the reducing atmosphere becomes an important technological issue.

This paper reports a study of the production of a carburizing atmosphere for surface treatment of steel from the partial oxidation of natural gas in a catalytic reactor. The reactor studied was a production size reactor with 300 mm of diameter and 1500 mm of length, packed with nickel-alumina catalyst. The reactor was originally built for producing reducing atmosphere from nitrogen-methanol.

The reactant mixture (natural gas and air) and reactor temperature were independently controlled in the reactor during typical production runs. The quality of the carburizing gas was measured from its dew point. The carbon potential of carburizing gas was calculated from the concentrations of carbon monoxide (CO), carbon dioxide (CO_2), oxygen (O_2) and methane (CH_4). These concentrations were measured at the exit of the reactor and were also predicted from gas-phase chemical equilibrium calculations.

The measured and calculated results indicate that CO concentration is very close to equilibrium, while CO_2 is higher and CH_4 is lower. These results were consistently reproduced for other operation conditions. Examining the reactor, it was possible to verify that there was an axial temperature gradient, resulting in lower residence time under the required processing temperature. This resulted in smaller decomposition of CH_4 and smaller production of CO_2 and explains the discrepancy between the experimental and simulation values. An equilibrium calculation of carbon potential (CP), expressed as weight percentage of carbon in iron, was developed to predict the possible optimizations of mixture composition and reactor temperature for a given required carbon potential.

To increase the carbon potential of the endothermic gas in the reactor two electric resistances were added to increase the temperature of the reaction. The results obtained were higher CP and a much higher output of endothermic gas. That change in the reactor made possible to generate a carburizing atmosphere under well-controlled and repeatable conditions for the carbon potentials required for surface carburizing of steels in industrial processing using natural gas and air mixtures. Equilibrium calculations matched well the measurements and allowed to establish the need for small diameter reactors and thicker thermal insulation, leading to uniform temperatures along the reactor; smaller percentage of stoichiometric air and increase in temperature to obtain higher carbon potentials. The adoption of higher temperature in the process using natural gas resulted in a significant reduction of production costs and an increase in process reliability.

TABLE OF CONTENTS

PAPER

Introduction

A carburizing process can be described as a surface treatment in which carbon, present in a carbon rich atmosphere, diffuses into iron or steel at around 900℃. When the metal is cooled rapidly by quenching, the higher carbon content on the outer surface becomes hard via the transformation from austenite to martensite, while the core remains soft and tough as a ferritic and/or pearlite microstructure. It produces workpieces that has a hard high carbon fatigue resistant surface and a low carbon core granting toughness and ductility.

The carbon content on the piece depends on the temperature and the composition of the atmosphere, therefore the carburizing process demands an adequate control of furnace atmosphere. This atmosphere must be rich in carbon monoxide (CO) and hydrogen (H_2), maintaining low levels of carbon dioxide (CO_2). The quality of the atmosphere is controlled by the carbon potential (CP) on the surface of the piece, which indicates the carbon content in equilibrium with iron for a given atmosphere at a given temperature.

The atmosphere in the furnace can be defined as an endothermic gas, a product of incomplete combustion in a controlled environment with reducing agents, CO and H_2, that shield surfaces from oxidation. The endothermic gas generating is done by injecting a mixture of air and natural into a nickel-alumina catalytic reactor, known as a retort. The walls of this reactor are maintained at a temperature of 1020 ℃ using electric heaters.

Results

The equipment studied was originally operated with propane and had been adapted for operation with natural gas. It was the first device of this type applied to carburizing to operate with natural gas in Brazil, therefore, an innovation in the industry. Overall the project was successful, however, since the original reactor was designed to operate on propane, some difficulties in the operation of natural gas retorts remained. The main problems encountered can be summarized in two items:

1. High content of CO_2 gas produced resulting in low carbon potential. It was found that the CO_2 content was around 0,6% and the potential of carbon between 0,25 and 0,30%. Correction of the carbon potential was done by injecting natural gas directly into the furnace, which increases the production of soot.

2. Due to low yield, the plant had two reactors to supply endothermic gas to nine furnaces at a nominal flow of 8 Nm^3/h per furnace. When all furnaces were connected, the desired carbon potential could not be maintained. By regulating the carbon potential to the appropriate value there was not enough flow to feed the nine furnaces. The current conditions of operation allowed only the operation of six or seven furnaces. The reducing atmosphere in the rest of the furnaces was supplied by a synthetic atmosphere (a mixture of methanol and nitrogen).

Figure 1 shows a sectional view of the retort, indicating the positions of the temperature measurement points. The gas temperature was obtained from a thermocouple (T1) located in the upper part of the catalyst bed and from the reactor temperature in a control thermocouple (T2) positioned next to the reactor walls. The gas composition was measured at the outlet of the retort after the primary heat exchanger (not shown in the drawing). The flow of air and natural gas were obtained through the rotameters installed in the machine.

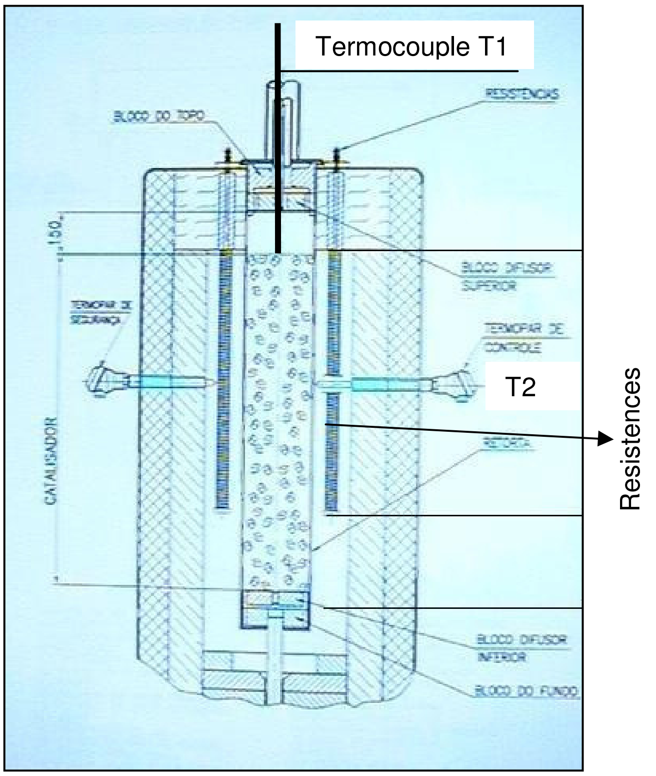

Figure 1. Schematic representation of the catalytic reactor (retort)

Table 1 presents the main measurements results. Six tests were performed with the retort in operation, the number of furnaces being fed by the endothermic gas varied. The CO_2 concentration remained lower than 0,30% in the first three tests. This behavior was considered odd by the operators of the equipment. In two subsequent tests the CO_2 concentration was above 0,50%, which is more representative of operating conditions typically found in the retorts. A probable cause of good operation in the early tests is the retort that had recently gone through the procedure of regeneration (which is done every weekend - the tests were conducted on Monday morning). Thus, in the first hours of operation, while the catalytic elements are more active, the CO_2 concentration is low. As the catalyst bed reduces its activity according to the actual operation of the equipment, the CO_2 concentration increases.

test	furnaces	Q_{ar}, Nm^3/h	Q_{GN}, Nm^3/h	CO, %	CO_2, %	CH_4, %	T1, ºC	T2, ºC	CP, %	%stoich. air
1	0	21,0	8,0	-	-	-	938	1020	-	25,6
2	2	18,7	7,8	20,20	0,29	0,27	867	1020	0,78	23,4
3	3	18,5	7,5	20,24	0,30	0,28	864	1020	0,79	24,1
4	4	18,3	7,6	20,68	0,20	0,40	866	1020	1,24	23,5
5	4*	17,5	6,8	20,37	0,51	0,26	857	1020	0,52	25,1
6	0	20,0	8,0	19,89	0,68	0,22	856	1020	0,37	24,4

Table 1. Measurements in retort #2

The temperature of endothermic gas at the outlet of the retort showed values around 860 ° C. These values are smaller than the programmed value for the temperature of the retort, which is 1020 ºC.

Additionally, Table 1 shows the values of carbon potential (CP), given by weight percentage of carbon dissolved in iron, and the values of the percentage of stoichiometric air. The carbon potential was calculated from concentration data of CO and CO_2 (or H_2 and CH_4), following the method of Yan (2001). The percentage of stoichiometric air means the percentage of air being used in relation to the amount of air necessary for complete combustion of fuel. The higher the percentage of stoichiometric air, the higher the amount of air there is in the mixture of reactants.

The CP was below 1% for most tests. Only in test number four CP peaked at 1.24%, however, operators felt that this test does not represent the normal operation of the machine, and it was probably an effect of the recent regeneration procedure.

The evaluation of the operation of retorts and consequently the carbon potential can be done by calculating the chemical equilibrium of the combustion products, ie, by determining the theoretical volumetric composition of the endothermic gas for a given condition of temperature and the reactants concentration. Further details about the equilibrium formulation can be found in Turns (2000).

As the reactor temperature is not constant and the residence time of gases within the reactor is not long enough, the gases generated are expected to not be in thermodynamic equilibrium. Another factor to consider is that the catalytic reactor can accelerate certain reactions, deviating the reaction from equilibrium. However, the assessment based on chemical equilibrium allows verifying the trends in the process and determine the theoretical limits for the composition of the various chemical species of interest.

Test 5	CO, %	CO_2, %	CH_4, %
Measured	20,37	0,51	0,26
Equilibrium	20,80	0,14	0,72

Table 2. Comparison between measurement and calculation of equilibrium condition for test 5

	Test 2		
	CO	**CO_2**	**CH_4**
Measured	20,20%	0,29%	0,27%
Equilibrium	20,85%	0,12%	0,67%
	Test 3		
	CO	**CO_2**	**CH_4**
Measured	20,24%	0,30%	0,28%
Equilibrium	20,86%	0,06%	1,38%
	Test 4		
	CO	**CO_2**	**CH_4**
Measured	20,68%	0,20%	0,40%
Equilibrium	20,88%	0,07%	1,14%
	Test 6		
	CO	**CO_2**	**CH_4**
Measured	19,89%	0,68%	0,22%
Equilibrium	20,67%	0,03%	2,74%

Table 3. Comparison between measurement and calculation of equilibrium condition

Table 2 shows the comparison between measurement and calculation of equilibrium condition for test number 5. The concentration of CO is close to that predicted by the chemical equilibrium while the concentration of CO_2 is more than the prediction and CH_4 is less than the prediction. These differences in the equilibrium are expected for the reasons outlined above. Appendix Table 3 presents the same comparison made for the other tests. However, it should be clear that these tests may show strong influence of the regeneration process as the retort was not operating at steady state.

Figure 2 shows the result of the calculation of chemical equilibrium as a function of reactor temperature for the operating condition of the test number 5. The chart is limited to major chemical species present in the combustion gases. Monoatomic oxygen, butane, propane and ethane, also considered in the calculations, have concentrations below 0.01% and therefore are not shown in the chart. Nitrogen gas, which is the most abundant species, can be calculated as the difference between 100% and the sum of the other species. The inclusion of other chemical species in the calculation of equilibrium, most of all, containing the chemical element carbon, are important only at temperatures above 1000 ℃ and therefore were not considered.

It is observed that as the reactor temperature increased the concentration of CO_2 and CH_4 decreased while the concentrations of CO and H_2 increased. On the other hand, the concentrations became flat at temperatures between 900 ºC and 1000 ℃.

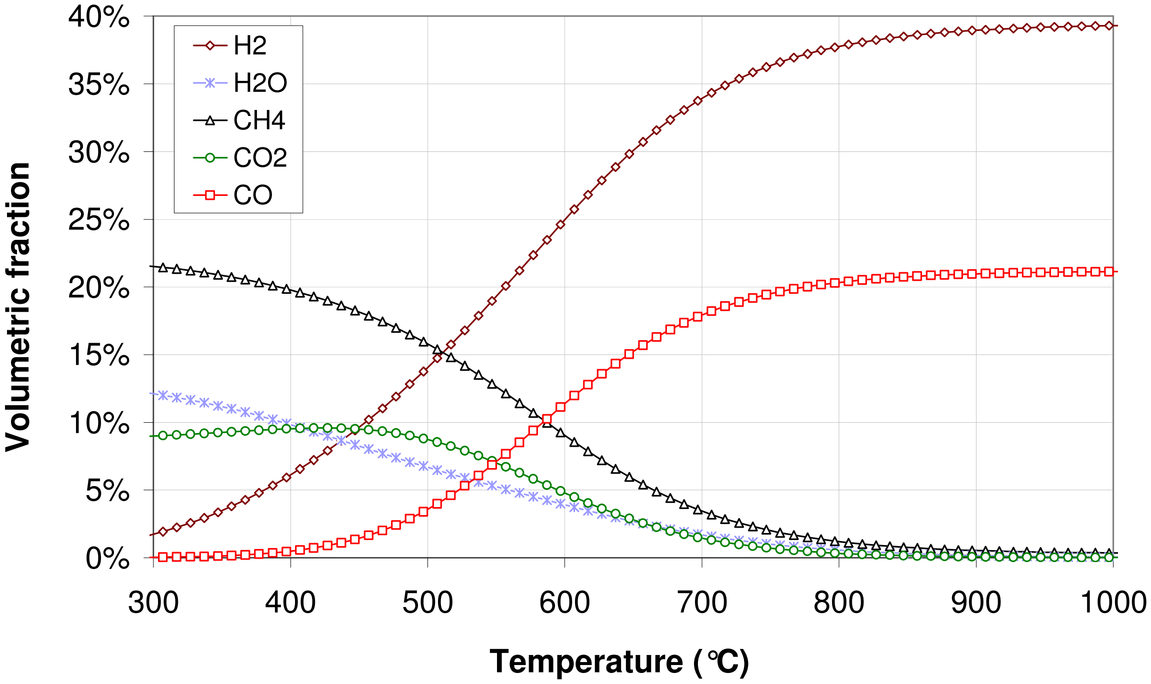

Figure 2. Equilibrium composition of the endothermic gas for the test condition No. 5 (Nm^3 / h = 6,8 QGN Qar = 17.5 Nm3 / h) as a function of reactor temperature.

Again using chemical equilibrium calculations, it is possible to determine the theoretical potential for carbon a given mixture of reactants. Figure 3 shows the carbon potential (CP) depending on the composition of the reactants and the reactor temperature to a pressure of 1 atm. Note that for any temperature the CP is greater as the percentage of stoichiometric air decreases. Regarding the temperature of the retort, there is a sharp increase in air esteq% for CP. above 24%. Below this level the CP tends to decrease with temperature.

Importantly, the results of Figure 3 are qualitative. As already mentioned, the endothermic gas produced by the retort is not in thermodynamic equilibrium, so the theoretical results presented serve as an indicator of trends that will be encountered in actual equipment. Note also that in Yan (2001) and other references consulted are not given the limits of validity of the equilibrium constants used in calculations of carbon potential.

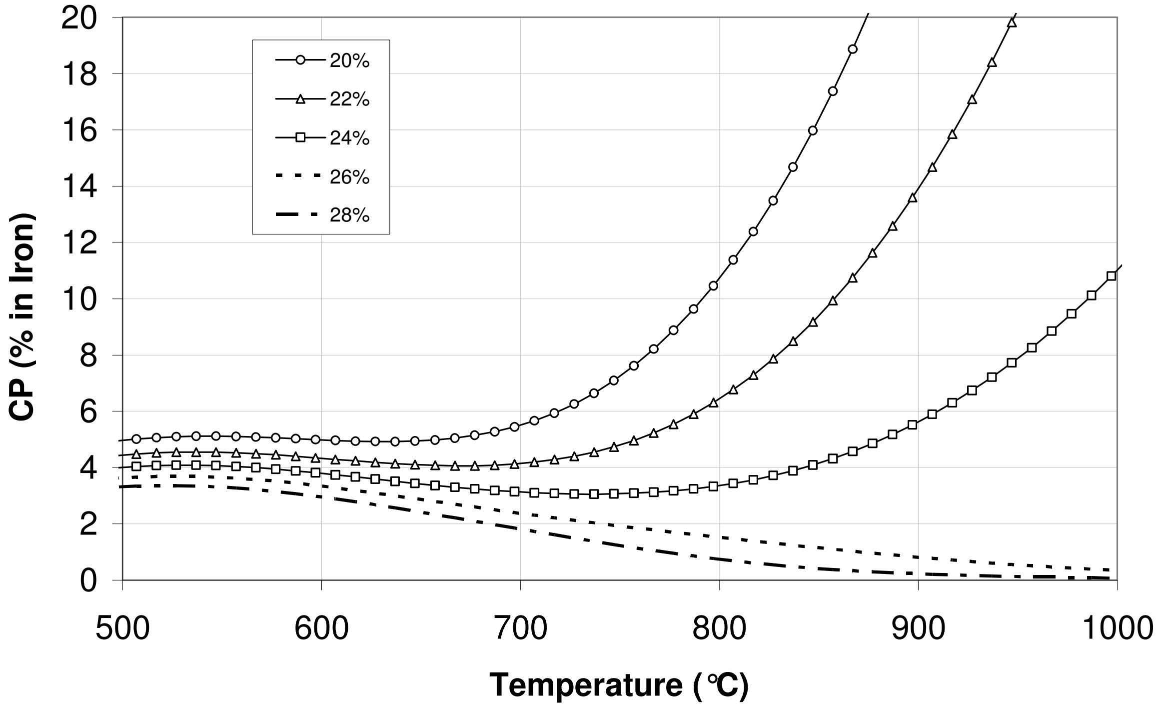

Figure 3. Carbon potential, given in percentage by weight of carbon in Iron, depending on the percentage of stoichiometric air and reactor temperature, at a pressure of 1 atm.

Based on these qualitative results it can be concluded that the operation of retorts should improve with the decrease in the percentage of stoichiometric air and increase with retort temperature. The combination of these two actions must be employed to increase the carbon potential of the endothermic gas.

To increase the carbon potential of the endothermic gas in the reactor two electric resistances were added to increase the temperature of the reaction. The results obtained were higher CP and a much higher output of endothermic gas with less CO_2 content. That change in the reactor made possible to generate a carburizing atmosphere under well-controlled and repeatable conditions for the carbon potentials required for surface carburizing of steels in industrial processing using natural gas and air mixtures. The adoption of higher temperature in the process using natural gas resulted in a significant reduction of production costs and an increase in process reliability.

	Before	**After**
CP (%)	0,30	0,38
CO_2 (%)	0,60	0,30
CO (%)	20%	20%
T (°C)	850	950
Q (Nm^3/h)	18	38

Table 4. Endothermic gas production output before and after the addition of electric resistances to increase reactor temperature

Table 4 summarizes the characteristics of the endothermic gas production before and after the inclusion of the electric resistances to increase the reactor temperature. The temperature increased about 100°C on average, resulting in higher quality workpieces, the carbon potential on the their surface increased from 0,30% to 0,38%. The CO_2 volumetric concentration decreased from 0,60% to 0,30%, the CO content remained at 20% and the flow had the largest influence, increasing from 18 Nm^3/h to 38 Nm^3/h. After the change, one reactor alone was able to feed the nine furnaces with quality endothermic gas.

Conclusion

This paper analyses the causes and presents the solution of an endothermic gas converted reactor with poor yield. The reactor originally operated on propane, but after the conversion to a lower cost raw material, natural gas, the endothermic gas produced resulted in low carbon potential on the metal pieces. The main conclusions of this work can be summarized on these two items:

1. Based on the analysis of chemical equilibrium results the operation of retorts should improve with the decrease in the percentage of stoichiometric air and with the increase of retort temperature.

2. Change in the length of the electric resistance led to an average increase of endothermic gas temperature of 100 ℃. This change has generated an improvement in the quality of the endothermic gas approaching the ideal composition, and also increasing notably the yield of volume of gas per hour, from 18 Nm^3/h to 38 Nm^3/h.

The results presented a successful use of natural gas as a raw material in a carburizing steel surface process in a process generally dominated by other fuels, representing a market expansion. As natural gas is cheaper than the traditional process, it grants its users a greater competitive advantage. The conversion of a propane catalytic reactor also represent a low cost solution by the re-utilization of an existing equipment.

REFERENCES

1. Yan, M. F. (2001), “Study on absorption and transport f carbon in steel during gas carburizing with rare-earth addition”, Material Chemistry and Physics, V. 70, pp. 242-244.

2. Turns, S. R. (2000), “An introduction to combustion – Concepts and applications.” 2ª Ed., Mcgraw-Hill.

3. Fox, R. W., McDonald, A. T., Pritchard, P. J. (2004), “Introdução à Mecânica dos Fluidos”, 6ª Ed., John Wiley & Sons.

LIST OF TABLES

LIST OF FIGURES