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Drip Feed Carburizing

By Urs Wyss

THE CARBOMAAG DRIP FEED METHOD of gas carburizing was developed in the late 1950's and early 1960's.^{1,4} It is now widely used in Europe and Japan.

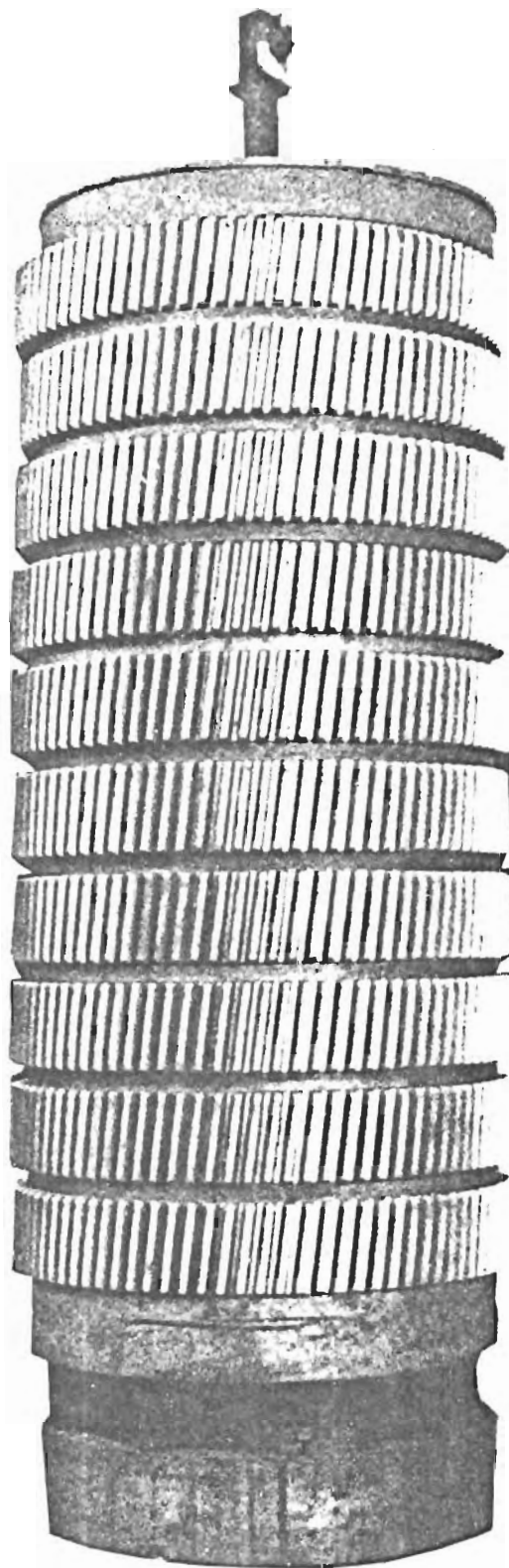
Basically, the drip feed method relies on methanol "carrier" and acetone or ethyl acetate "carburizer" liquids instead of conventional endothermic gas. As a result, applications tend to be found in areas where no natural gas is available (or its cost is very high), or where an alternative to conventional carburizing is desirable.

The two liquids are simultaneously, but separately, introduced into the furnace. The methanol cracks to form a gas which scavenges the furnace and then provides the desired positive pressure during the carburizing cycle. The acetone or ethyl acetate cracks to produce the gas necessary for setting the desired carbon potential.

Most of the furnaces set up for Carbonaag heat treating are pit and pot-type furnaces. The technique can, however, also be adapted to horizontal batch furnaces with integral oil quenchers and to continuous furnaces. The largest drip feed carburizing furnaces in operation today have usable dimensions of 6.5 ft (2 m) diameter and 9 ft (2.7 m) depth, and 3.5 ft (1 m) diameter and 17 ft (5.2 m) depth. There is no upper dimensional limitation on the process.

Other major advantages of the process:

1. A carbon potential controllability equal to that of conventional endothermic gas carburizing.
2. Elimination of the need for an endothermic gas generator.
3. A higher carbon availability per unit volume, which promotes more uniform carburizing of blind holes and other hard-to-carburize areas, and assists in the carburizing of high-density work loads.
4. A higher carbon transfer coefficient which translates into somewhat shorter carburizing times.



Load of 10 locomotive engine gears of 900 mm (3 ft.) diam containing spring pockets, ready to be carburized according to the Carbonaag method (see Example 2, Fig. 5, and Table III.)

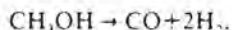
5. Reduced amounts of waste combustible gases.

6. No need to continue the production of carburizing gases between different carburizing cycles.

The Carbonaag method was originally designed for carburizing steels and for heating steels with medium to high carbon contents to hardening temperatures above 840 C (1545 F) under an atmosphere with controlled carbon potential. Now, lower carbon grades can also be processed at lower temperatures by adding a controlled amount of nitrogen. With an ammonia addition, carbonitriding can be performed. The system's flexibility is such that neutral hardening and annealing are also possible by substituting pure nitrogen.

Details on Cracking Kinetics and Carburizing Reactions

The liquid methanol cracks into carbon monoxide and hydrogen:



Although the methanol replaces the conventional carrier gas, its most important function is to maintain a positive pressure inside the furnace at all times, including those when the flow of carburizer is interrupted. The carburizing effect of the methanol is extremely small because its feed rate is very low, 200 to 400 g/h (0.4 to 0.9 lb/h).

The carburizer is selected to produce roughly the same gas composition, via its cracking and carburizing reactions, as that produced by cracking methanol. This condition must be satisfied to ensure that the total furnace gas composition remains constant, allowing automatic control of the carburizer's feed rate by controlling the carbon dioxide content or water content (dew point) of the furnace gas.

The cracking reaction of methanol and the CO content (33%) of the resulting gas is shown at the left of Fig. 1. At the

right are ideal carburizing reactions for ethyl acetate and acetone, the carburizers of major interest, and data points indicating the resulting CO contents. The graph includes all ratios of mixtures, from pure methanol to pure carburizer. Note that ethyl acetate, when fed in any portion with methanol, produces no deviation from the basic gas composition. Experience, however, has shown that the deviations produced by acetone are so small that this less expensive and easily crackable liquid can also be used as the carburizer.

Other organic liquids and pure hydrocarbons cause such large deviations from the basic gas composition that carbon potential control by carbon dioxide or dew point measurements is essentially impossible.

Reaction Rates: We used gas chromatography to analyze furnace gas compositions during the carburizing of many loads having very different surface areas. Our data indicate that cracking reactions within the furnace are extremely fast and that the succeeding homogeneous gas reactions and the carburizing reactions are slower. The conclusion: as carburizer feed rate (that is, surface area) increases, the products of the primary cracking reaction tend to be enriched in the furnace gas, causing some deviation in the basic gas composition.

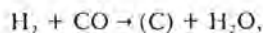
Figure 2 gives the cracking reactions for ethyl acetate and acetone, and the succeeding homogeneous gas reactions and carburizing reactions. Methane (CH_4) formed by cracking either carburizer, and CO , formed only by cracking ethyl acetate (or by one of the carburizing reactions) react with each other relatively slowly. Thus, these compounds may attain rather high concentrations above equilibrium if the feed rate is high, as is the case when carburizing large surface areas.

Under these circumstances, the carbon potential of a

methanol-ethyl acetate process cannot be safely controlled by measuring CO_2 content because the gas is not in equilibrium. Dew point control of carbon potential is, however, possible.

In a methanol-acetone process, CO_2 control can be used because cracking acetone does not produce carbon dioxide.

In either process, the predominant carburizing reaction appears to be:



seemingly the fastest of the three indicated in Fig. 2.

Controllability of the Carbon Potential

It has been pointed out that the basic gas composition must remain essentially constant for the carbon potential to be automatically controlled by CO_2 content or dew point. Additional factors that need to be considered include the kinetics of the cracking and subsequent reactions.

For example, consider the entire range of methanol-ethyl acetate and methanol-acetone mixtures. Next, assume that the carburizers are fed according to the instantaneous carbon demand of the surface, maintaining, for example, a carbon potential of 1% at 920 C (1690 F). Experience shows that large amounts of methane are produced — in extreme cases, more than 10 times the equilibrium content — as carburizer feed rates increase. And, if ethyl acetate is used as the carburizer, CO_2 contents will also be above equilibrium.

The allowable change of the basic gas composition can be evaluated by examining the influence of the possible variation of the square of the partial pressure of CO ($p^2\text{CO}$) on the carbon potential at a constant CO_2 content, or the influence of $p\text{CO} \times p\text{H}_2$ at a constant dew point.

Here's what's observed under dew point control: with increasing CH_4 contents (higher portions of carburizers), larger negative deviations of $p\text{CO} \times p\text{H}_2$ result from both ethyl acetate and acetone than would be expected under idealized conditions. The deviation of $p^2\text{CO}$ for ethyl acetate becomes rather large and is positive; for acetone, the deviation is negative.

Under actual conditions, the content of carburizer (controlled by the instantaneous carbon demand) varies within a working range of 15 to 90%. Within this range, the $p\text{CO} \times p\text{H}_2$ values for methanol-ethyl acetate vary between 0.212 and 0.192; for methanol-acetone, between 0.210 and 0.172. These values correspond to a shift of the carbon potential from 1.00 to 0.93% for methanol-ethyl acetate and from 1.00 to 0.87% for methanol-acetone. Taken one step further, they correspond to deviations of ± 0.035 and $\pm 0.065\%$ C respectively.

Over the whole range of 0 to 100% carburizer, the devia-

tion from a mean value would be $\pm 0.055\%$ C for ethyl acetate and $\pm 0.105\%$ C for acetone. Theoretically, these are the largest possible deviations, and do not appear in practice.

Under CO_2 control, the deviations from a mean set point are $\pm 0.055\%$ C for ethyl acetate and $\pm 0.065\%$ C for acetone within the carburizers' 15 to 90% working range. For the full range (0 to 100% carburizer), the deviations are ± 0.08 and $\pm 0.10\%$ C respectively.

Note that the ethyl acetate values have only a limited meaning because of the possibility that the CO_2 content is above equilibrium. It's for this reason that acetone is preferred if CO_2 control is desired. In practice, the $\pm 0.065\%$ C deviation for acetone can be reduced by using a mixture of 75% acetone and 25% ethyl acetate.

Conventional Process: Similar data for the endothermic gas process have also been developed. The variations of $p\text{CO} \times p\text{H}_2$ and $p^2\text{CO}$ were calculated as a function of the carrier gas/natural gas ratio, which was assumed to have a working range between 30 and 8. The product of $p\text{CO} \times p\text{H}_2$ remains nearly constant up to ratios far below this limit because of the opposite changes of H_2 and CO contents (as the carrier gas/natural gas ratio decreases, H_2 increases rapidly at the expense of CO and N_2). As a result, the shift of carbon potential at a constant dew point is very small ($\pm 0.025\%$ C).

In contrast, $p^2\text{CO}$ decreases fast with decreasing carrier gas/natural gas ratios. Within the working range, $p^2\text{CO}$ varies from 0.037 to 0.026, causing a carbon potential shift from 1.00 to 0.79% C at a constant CO_2 content. This corresponds to a deviation of $\pm 0.105\%$ C.

Over the whole range, from carrier gas without enriching gas to a carrier gas/natural gas ratio of 8, the carbon potential would shift from 1.00 to 0.73% — relatively small changes in the ratio cause large deviations of the carbon potential at a constant CO_2 content.

The data given above on Carbomaag and conventional carburizing are summarized in Table I. The deviations are the largest possible and can easily be reduced in practice by adapting the set point to the working conditions.

Bear in mind that the very low dew points and CO_2 contents of the endothermic gas process are much more difficult to reliably control than are the higher ones of the Carbomaag process. The advantage of the carbon potential's insensitivity to changes in the carrier gas/natural gas ratio when dew point is used is therefore limited. From the point of view of gas composition variability, carbon potential can be well controlled within the working range of both processes. However, the working range of the Carbomaag process is very large, whereas that of the endothermic gas

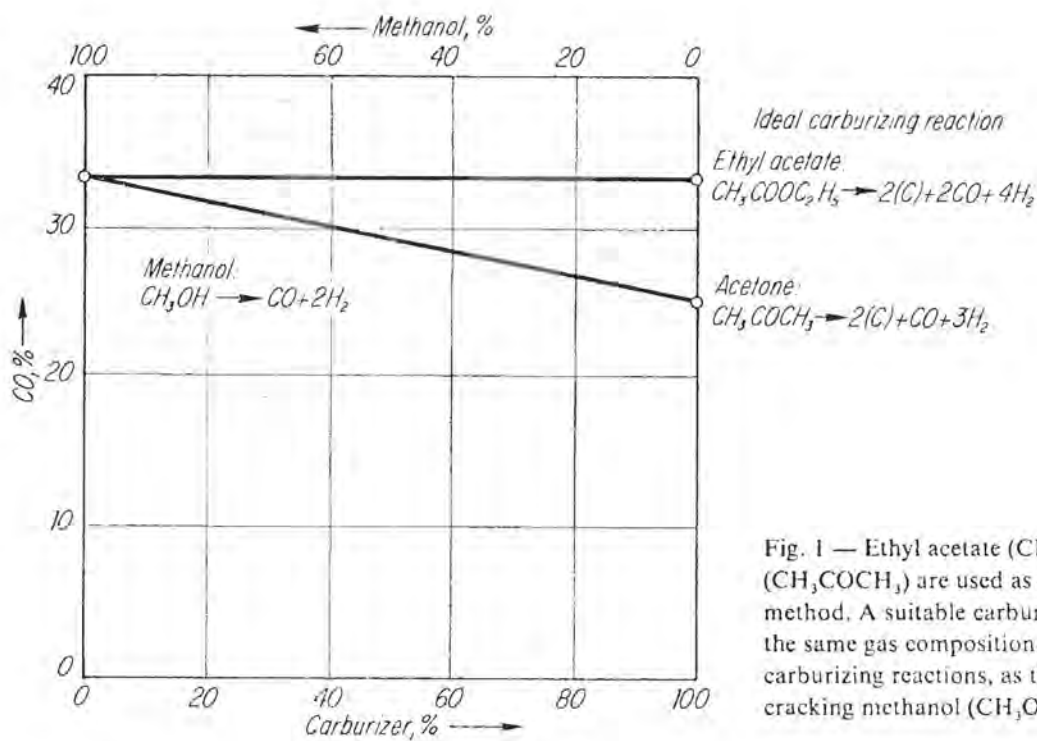


Fig. 1 — Ethyl acetate ($CH_3COOC_2H_5$) and acetone (CH_3COCH_3) are used as carburizers in the drip feed method. A suitable carburizer must produce roughly the same gas composition, via its cracking and carburizing reactions, as that produced by cracking methanol (CH_3OH).

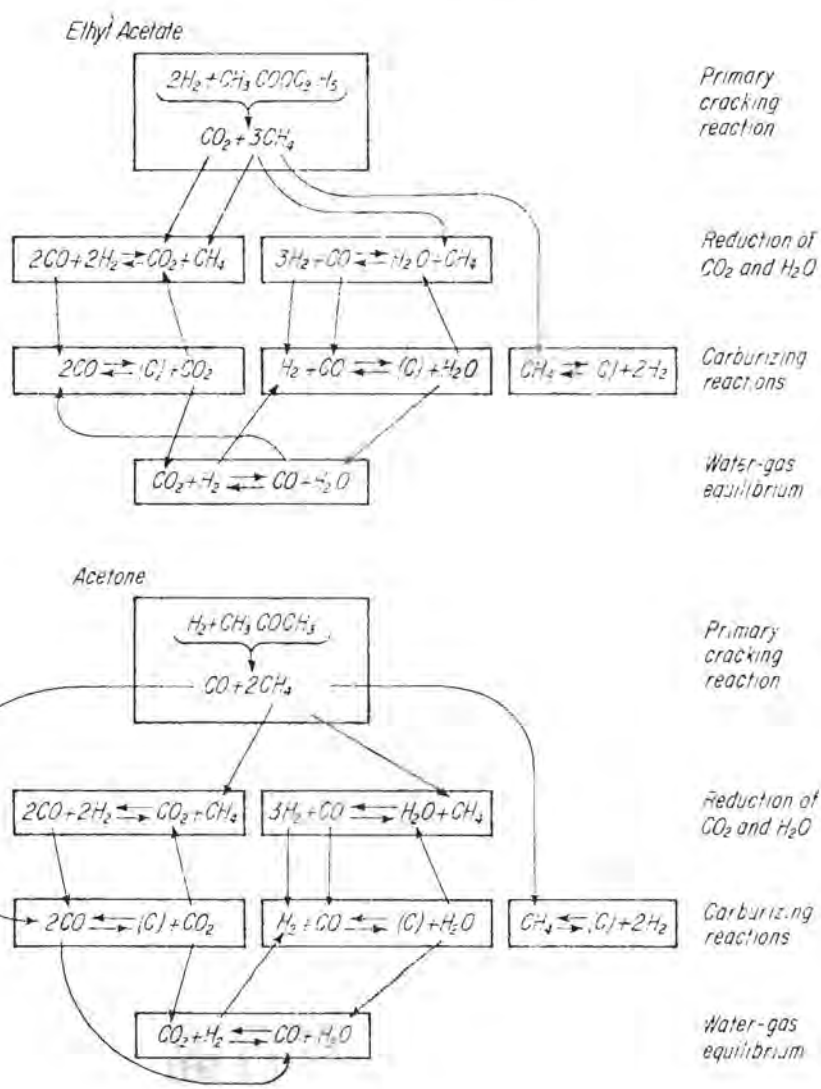


Fig. 2 — Cracking, homogeneous gas, and carburizing reactions for ethyl acetate and acetone are diagrammed here. The predominant carburizing reaction is $H_2 + CO \rightarrow (C) + H_2O$.

Table I — Maximum Carbon Potential Deviations For Various Carburizing Processes¹

Carburizing Process	Dew Point Control		CO ₂ Control	
	Working Range	Full Range	Working Range	Full Range
Methanol-ethyl acetate	±0.035	±0.055	±0.055 ²	±0.08 ²
Methanol-mixture of 75% acetone + 25% ethyl acetate	±0.045	±0.075	±0.05	±0.08 ²
Methanol-acetone	±0.065	±0.105	±0.065	±0.10
Endothermic gas	±0.025	Out of control	±0.105	Out of control

1. Highest possible deviation of carbon potential from a mean set point of approximately 1% C at 920 C (1690 F) caused by changes in the basic gas composition.
2. CO₂ control not recommended for production applications.

process is very narrow and can only be maintained by excessive carrier gas.

Carbon Data: The carbon availability of a carburizing atmosphere can be defined as the amount of carbon transferred to the steel surface by a given volume of gas while the carbon potential is reduced from 1.00 to 0.90%.³ To obtain an "absolute" value, the difference in CO₂, H₂O, and CH₄ contents in equilibrium at carbon potentials of 1.00 and 0.90% has to be taken into account. To calculate an "effective" carbon availability, however, CH₄ can be disregarded — this gas is not directly involved in carburizing because of its slow reaction rate.

It has been calculated, for example, that the effective carbon availability of the Carbomaag process is 2½ times higher than that of the endothermic gas process. This higher carbon availability is an advantage when carburizing blind holes and other areas poorly exposed to the circulating gas, and when carburizing charges having high load densities.

Carbon transfer coefficients are also higher by roughly the same amount: 275 × 10⁻⁷ cm/s for methanol-ethyl acetate versus 120 × 10⁻⁷ cm/s for endothermic gas. The practical effect is shown in Fig. 3, where the growth of a carburized case at 930 C (1705 F) on a 0.15C, 3.5Ni, 0.75Cr alloy steel is plotted for both carburizing methods. The difference in case depth at a given carburizing time is caused by the difference in the carbon transfer coefficients. The comparison reveals that the difference, when expressed as a

percentage time reduction, increases in importance as case depth decreases. On the other hand, the absolute decrease in carburizing time increases with increasing case depth. Example: for a 0.020 in. (0.51 mm) case, the time saving using the Carbomaag process is 27% or 30 min; for a 0.080 in. (2.03 mm) case, the gain is 9% or 95 min.

Comparing Carburizing Cycle Inputs and Outputs

The input of carburizing agents in any form, the output of carbon which is absorbed by the steel surface, and the amount of waste gases which need a corresponding volume of air for combustion can easily be compared by analyzing the amount of carbon involved in the carburizing process and its relation to the amount of carbon absorbed (or to the case depth).

For example, the production of endothermic gas from natural gas (CH₄) and the effect of the enriching gas can be expressed in a simplified manner:



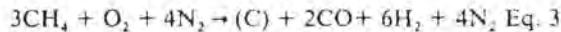
Or, 2 mol of methane plus 5 mol of air gives 10 mol of carrier gas containing 6 mol of combustible gases.

The carrier gas/enriching gas ratio is ten to one:



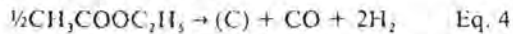
In equation 2, (C) represents the carbon absorbed by the surface.

Adding equations 1 and 2 gives:



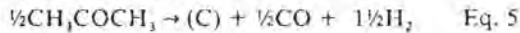
Or, for 1 mol of carbon absorbed by the steel, 3 mol methane have to be supplied and 8 mol combustible gases are lost which need 20 mol air for combustion.

The ethyl acetate reaction is:



Or, 2 mol of carbon are involved when 1 mol carbon is absorbed; and 3 mol of combustible gases are produced requiring 7.5 mol air for combustion.

The acetone reaction is:



Or, $1\frac{1}{2}$ mol of carbon are involved when 1 mol carbon is absorbed; and 2 mol of combustible gases are produced requiring 5 mol air for combustion.

In the Carbomaag process, the amount of methanol per unit carbon absorbed by the surface is extremely small for a high demand of carburizer (large surface) and is relatively large for a small demand of carburizer (small surface). Thus, any comparison between processes must be based on distinct surface areas to be carburized.

Example 1: In Fig. 4, a surface area of 43 ft^2 (4 m^2) was assumed and a case depth of 0.050 in. (1.3 mm) — referred to as 0.30% C — had to be obtained for SAE 8620 ring gears at a carburizing temperature of 1700 F (925 C).

Case depth at dph 550, mm (.in.)

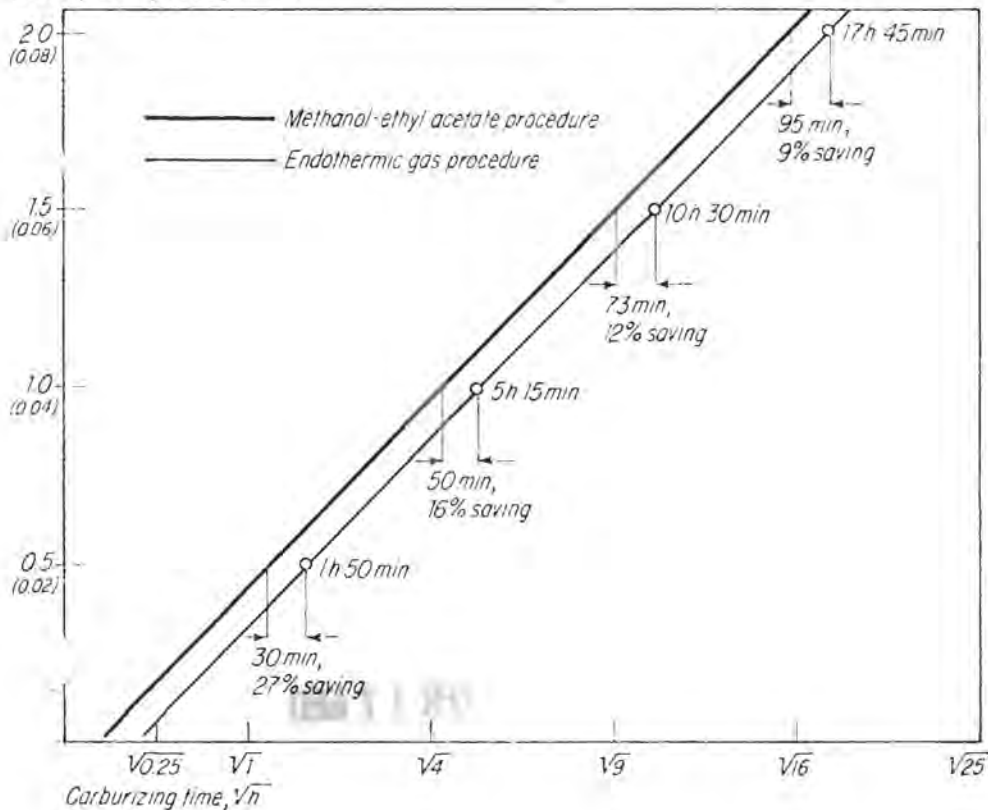


Fig. 3 — Shorter carburizing times are one advantage of the Carbomaag process over conventional endothermic gas carburizing. Absolute and percentage time savings are shown here for a number of case depth-carburizing time combinations. Steel: 0.15C, 3.5Ni, 0.75Cr. Temperature: 930 C (1705 F). Carbon potential: 1.15% C.

Table II — Input-Output Comparison for Carburizing a Small Surface Area (see Fig. 4)¹

Input/Output	Endothermic Gas	Methanol-Acetone
Input		
Carrier gas	675 ft ³ (19 m ³)	—
Natural gas (enriching)	36 ft ³ (1.0 m ³)	—
Methanol	—	4.69 lb (2.1 kg)
Acetone	—	1.23 lb (0.6 kg)
Carbon involved	5.72 lb (2.6 kg)	2.5 lb (1.1 kg)
Carburizing time	6 h 45 min	5 h 55 min
Output		
Carbon absorbed by surface	0.44 lb (0.2 kg)	0.44 lb (0.2 kg)
H ₂	342 ft ³ (9.7 m ³)	127 ft ³ (3.6 m ³)
CO	134 ft ³ (3.8 m ³)	60 ft ³ (1.7 m ³)
H ₂ + CO	476 ft ³ (13 m ³)	187 ft ³ (5.3 m ³)
Necessary air for combustion	1192 ft ³ (34 m ³)	468 ft ³ (13 m ³)
Lost heat of combustion	154 434 Btu (163 MJ)	60 567 Btu (64 MJ)

1. Surface area of 43 ft² (4 m²) carburized at 1700 F (925 C) to a case depth of 0.050 in. (1.3 mm), or 0.30% C. Steel: SAE 8620.

Table III — Input-Output Comparison for Carburizing a Large Surface Area (see Fig. 5)¹

Input/Output	Endothermic Gas	Methanol-Acetone
Input		
Carrier gas	5130 ft ³ (145 m ³)	—
Natural gas (enriching)	264 ft ³ (7.5 m ³)	—
Methanol	—	14.1 lb (6.4 kg)
Acetone	—	23.15 lb (11 kg)
Carbon involved	43.2 lb (20 kg)	19.8 lb (9.0 kg)
Carburizing time	25 h 45 min	24 h
Output		
Carbon absorbed by surface	8.7 lb (3.9 kg)	8.7 lb (3.9 kg)
H ₂	2578 ft ³ (73 m ³)	756 ft ³ (21 m ³)
CO	1024 ft ³ (29 m ³)	307 ft ³ (8.7 m ³)
H ₂ + CO	3602 ft ³ (102 m ³)	1063 ft ³ (30 m ³)
Necessary air for combustion	9000 ft ³ (255 m ³)	2657 ft ³ (75 m ³)
Lost heat of combustion	1 167 000 Btu (1231 MJ)	344 000 Btu (363 MJ)

1. Surface area of 430 ft² (40 m²) carburized at 1690 F (920 C) to a case depth of 0.100 in. (2.5 mm), or 0.30% C. Steel: 15 CrNi6 (0.15C, 1.5Cr, 1.5Ni).

Solid lines pertain to the endothermic gas process and were derived from an ASM publication.⁶ The entire cycle, including a 1½ h heat-up took 6¼ h. Throughout the cycle, 100 ft³/h (2.8 m³/h) carrier gas was applied, and the addition of 12 ft³/h (0.3 m³/h) natural gas started when the carburizing temperature was reached and was then shut off after 3 h. Point A represent the total carbon involved in the endothermic gas process: 5.72 lb (2.6 kg). Total carbon absorbed: 0.44 lb (0.2 kg).

Dashed lines pertain to the Carbomaag process. Less than 6 h are needed for the whole cycle. The total carbon involved (pont B) is 2.5 lb (1.1 kg).

A more complete comparison of the two processes is given in Table II. Note that 2.5 times more combustible gases are developed by the endothermic gas process. This means that a correspondingly larger combustion heat is lost and much more shop air is used up.

Carrier gases lost when endothermic process furnaces are

not in use have not been taken into account. In the Carbomaag process, the flow of carburizer liquid can be shut off during these periods for an added saving.

Example 2; Figure 5 compares carburizing cycles for ten locomotive engine gears measuring 3 ft (0.9 m) in diameter with a total surface area of 430 ft² (40 m²). A case depth of 0.100 (2.5 mm) — referred to as 0.30% C — had to be obtained at 920 C (1690 F). The steel is 15 CrNi6 (0.15C, 1.5Cr, 1.5Ni).

Carburizing time was 24 h for the methanol-acetone process, and 25 h, 45 min for the endothermic gas process (heat-up times not included).

More details are given in Table III. In addition to a shorter carburizing time, the Carbomaag process also produces less than one-third of the combustible gases produced by the endothermic process. We feel that the lost combustion heat of the waste gases produced by the endothermic process amounts to 90% of the heat of com-

bustion of the natural gas supplied to the generator and to the furnace as enriching gas, not to mention the energy consumed by the generator itself.

Thus, the Carbonaag process is seen to be advantageous from an energy saving and environmental standpoint.

It should be pointed out that for the example in Fig. 5 and Table III, the carrier gas flow in the endothermic process was held at an unusually low level. Under typical production conditions, carrier gas flow rates would be substantially higher, and the energy/environment advantage of the Carbonaag process would be made even more dramatic.

Let me also emphasize that the supply of organic liquids can be shut off immediately after a cycle ends -- endothermic generators are producing carrier gas whether it's needed or not.

Using Nitrogen and Ammonia in the Drip Feed Process

The Carbonaag method can also be combined with nitrogen (100% N_2 for neutral hardening or annealing) or ammonia (for carbonitriding).

A nitrogen addition in carburizing applications would normally represent an unnecessary complication and a reversion to some of the disadvantages associated with the endothermic gas process. However, if low hardening temperatures (below 840 C [1545 F]) have to be used under a controlled carbon potential, a nitrogen dilution is needed to reduce the excessively high dew points required by the undiluted H_2 -CO mixtures produced by methanol. This is particularly true if the gas has to be in equilibrium with the carbon in low-carbon steels.

In the above case, accurate control of feed rates for the two organic liquids and the nitrogen gas are essential to maintain a constant gas composition.

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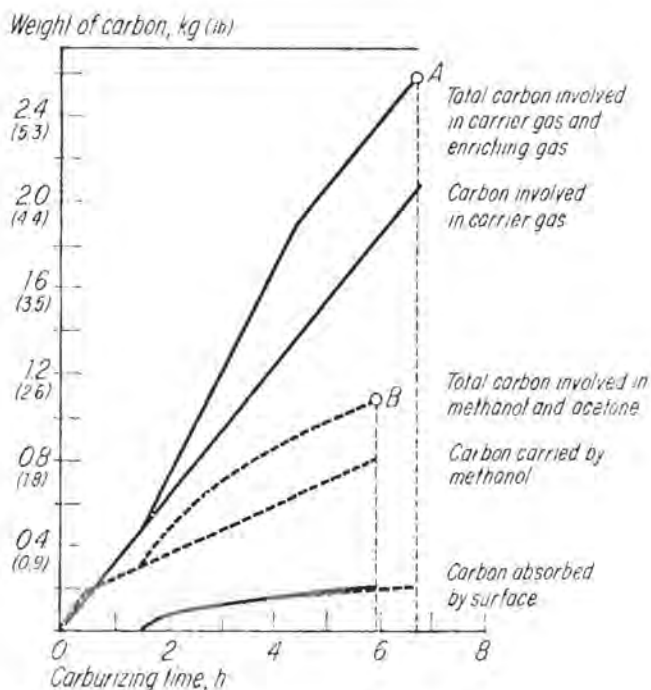


Fig. 4 — Comparison of the carbon needed to carburize a 43 ft² (4 m²) surface area of SAE 8620 steel by both drip feed and conventional methods. A detailed input-output comparison is given in Table II.

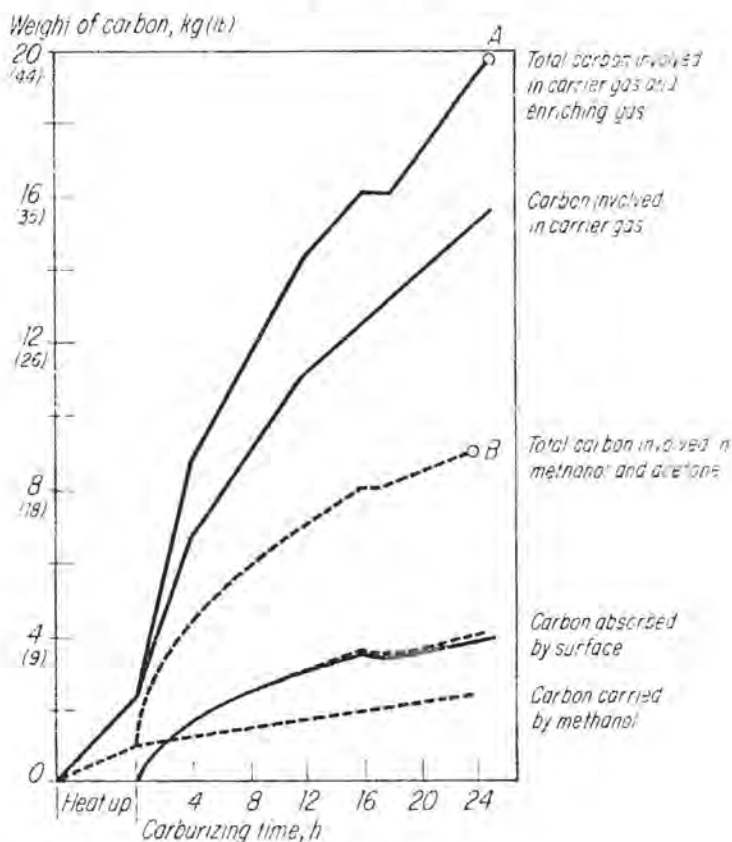


Fig. 5 — Comparison of the carbon needed to carburize a 430 ft² (40 m²) surface area of 15 CrNi6 steel (0.15C, 1.5Cr, 1.5Ni) by both drip feed and conventional methods. A detailed input-output comparison is given in Table III.