CARBON BLACK

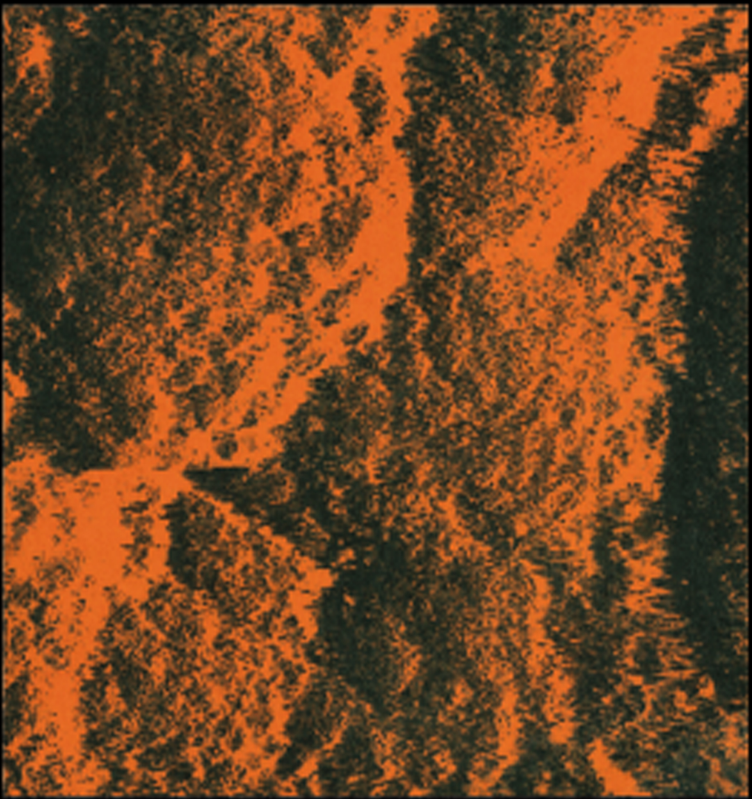
Second Edition, Revised and Expanded

edited by

Jean-Baptiste Donnet

Roop Chand Bansal

Meng-Jiao Wang



Science and Technology

CARBON BLACK
Science and Technology

Second Edition,
Revised and Expanded

edited by

Jean-Baptiste Donnet
Centre de Recherches sur la Physico-Chimie
des Surfaces Solides, CNRS
Mulhouse, France

Roop Chand Bansal
Panjab University
Chandigarh, India

Meng-Jiao Wang
Degussa AG
Hürth, Germany

Taylor & Francis
Taylor & Francis Group
Boca Raton London New York

CRC is an imprint of the Taylor & Francis Group,
an informa business

Library of Congress Cataloging-in-Publication Data

Carbon black / edited by Jean-Baptiste Donnet, Roop Chand Bansal, Meng
-Jiao Wang. -- 2nd ed, rev. & expanded.
p. cm.
Includes bibliographical references and index.
ISBN 0-8247-8975-X
1. Carbon-black. I. Donnet, Jean-Baptiste. II. Bansal,
Roop Chand. III. Wang, Meng-Jiao.
TP951.C34 1993
662'.93--dc20 93-16640
CIP

MARCEL DEKKER, INC.
270 Madison Avenue, New York, New York 10016

Current printing (last digit):
13 12 11 10

FOREWORD

“**Carbon Black**”, published in 1976 and written with Andy Voet and the help of my coworkers, has been “sold out” for many years and from many sides, academic and industrial, I was urged to prepare a second, updated edition.

I decided to prepare an edited book, with chapters by several colleagues and friends, most being authorities in this field, who accepted the task of writing separate, well documented chapters which make the new “**Carbon Black**”, I believe, a comprehensive reference book. I express my thanks to every coworker.

It was not easy to succeed in collecting the chapters, editing and preparing the book, and I wish to express my deepest gratitude to Roop C. Bansal and Meng-Jiao Wang, colleagues, friends and working as co-editors; without them the present edition would never have reached completion.

It is my hope that this work will serve the scientific and industrial “Carbon Black” community.

Jean-Baptiste Donnet

PREFACE

Carbon black is a fascinating material which has not only engaged the attention of those who are concerned with the technology and applications of this material but has also inspired a large number of fundamental investigations in scientific laboratories of universities and research institutes around the world.

Carbon black is widely used as a filler to modify the mechanical, electrical and optical properties of the medium in which it is dispersed. These applications play a major role in elastomers, plastics and in paints and inks. It is, therefore, hardly surprising that the literature on carbon black and its applications is extensive and is scattered in rubber, paint and printing ink trade journals, in general scientific and technical journals, and in periodicals covering such specialised subjects as Colloid Chemistry, Rheology, Polymer Chemistry, Material Science, Carbon, etc.

Since publication of the first edition in 1976, a huge amount of research work has been carried out using latest innovations such as FTIR, ESCA, inverse gas chromatography and STM. The examination of carbon black surfaces by these methods has led to a better understanding of the processing and the applications of this material as a filler. The discovery of fullerenes has given a new twist to the mechanism of carbon black formation, while STM has enabled scientists to have a look at carbon black structure on the atomic scale.

The literature on carbon blacks is so diverse that it appears beyond the capacity of a single author to justify all the subjects that need to be discussed in a book on carbon blacks. Consequently, an attempt has been made to collect chapters for the book from experts in their own fields and arrange them in one cover after suitable editing. Many of the theories and concepts presented in the first edition have been reviewed only briefly and more emphasis has been focussed on more recent investigations.

The book comprises 14 chapters discussing carbon black manufacture, the mechanism of its formation, its microstructure, morphology, physical and other properties, the chemical structure of carbon black surface, its fractal geometry and the role of carbon black in elastomers, plastics and xerographic toners. There are separate chapters on STM, surface energy, conductivity and health effect of carbon blacks while the role of carbon black in elastomers has been discussed in three different chapters. The book, thus, is expected to initiate scientists and technologists working in research centres and industry to take full advantage of the recent innovations and to have access to the relevant literature.

The manufacture of carbon blacks which include furnace, thermal, channel and acetylene blacks is discussed in the first chapter. Furnace blacks are made in a furnace by partial combustion of hydrocarbons. Channel blacks, which are now a very small part of the market, are manufactured by impingement of natural gas flames on channel irons. Thermal blacks are produced by thermal decomposition of natural gas, while acetylene black, a special type of thermal black, is made by exothermal decomposition of acetylene. The chapter describes the various processes along with the latest developments in the choice of the source materials and the factors influencing the optimum yield of carbon blacks. The mechanism of carbon black formation based on recent developments including the discovery of fullerenes is discussed in chapter 2.

The next four chapters deal with the microstructure, physical and other properties as well as the porous and chemical structure of the carbon black surface; the microstructure, morphological and other physical properties of carbon blacks are discussed in chapter 3, while chapter 5 provides a look at the atomic scale microstructure of carbon blacks by scanning tunnelling microscopy. The modification of carbon black surface by the formation of different types of surface chemical groups, their estimation and their influence on the physico-chemical behaviour of carbon blacks is the subject matter of chapter 4 and the influence of these chemical surface groups and microstructure on the basis of surface energetics is discussed in chapter 6.

There is a separate chapter each on fractal geometry and conducting carbon blacks. The concept of fractal geometry, as applied to agglomerate morphology and the interaction of carbon black with polymer, is dealt with in chapter 7. Chapter 8 discusses the influence of carbon black properties such as particle size and aggregate size on the conductivity of polymer-carbon black compounds. The mechanism of conductance in these compounds is also discussed.

The following five chapters are devoted to the applications of carbon blacks in elastomers (chapter 9–11), plastics (chapter 12) and xerographic toners (chapter 13). Chapter 9 discusses in detail the parameters of carbon black which govern their reinforcing ability in rubber. The factors such as interfacial interaction between rubber and carbon black, occlusion of the polymer in the internal voids of the aggregate and the agglomeration of the carbon black aggregates in the polymer matrix which determine their reinforcing behaviour are outlined, while chapter 10 discusses the fracture of carbon black filled vulcanizates at high temperature and under swollen conditions. Chapter 11 deals with the dynamic viscoelastic properties of carbon black loaded elastomers. The influence of carbon black properties on its applications in plastics to obtain compounds with excellent UV protection, SMI and antistatic shielding are discussed in chapter 12 while the influence of surface acidity and dispersion properties of carbon blacks on its performance in copiers and printers is considered in chapter 13.

Finally, the health effects of carbon black, a very important topic, are dealt with in chapter 14.

We express our thanks to the authors of different chapters who, at no small inconvenience, agreed to our request to write for the book. Professor Roop C. Bansal acknowledges his thanks to the CNRS Centre Mulhouse for the financial support and to Professor Schultz and Dr. Derai for making his stay comfortable. Professor Bansal also appreciates the patience and understanding of his wife Rajesh and daughters Meenakshi and Nidhi, who stayed in India during the several months that he spent in Mulhouse for the preparation of the book.

Jean-Baptiste Donnet
Roop Chand Bansal
Meng-Jiao Wang

CONTENTS

Chapter 1

Chapter 2

Chapter 3

Chapter 4

Chapter 5

Chapter 6

Chapter 7

Alain Le Méhauté, Michel Gerspacher and Claude Tricot

Chapter 8

Nicolas Probst

Chapter 9

Siegfried Wolff and Meng-Jiao Wang

CONTRIBUTORS

Roop Chand Bansal
Department of Chemical Engineering and Technology, Panjab University, Chandigarh, India.

Anil K. Bhowmick
Rubber Technology Centre, Indian Institute of Technology, Kharagpur, India.

Emmanuel Custodéro
Ecole Nationale Supérieure de Chimie de Mulhouse, Mulhouse, France.

Jean-Baptiste Donnet
Centre de Recherches sur la Physico-Chimie des Surfaces Solides, CNRS, Mulhouse, France.

John M. Funt
Billerica Technical Center, Cabot Corporation, Billerica, Massachusetts, U.S.A.

Michel Gerspacher
Fort Worth Research Center, Sid Richardson Carbon & Gasoline Co., Fort Worth, Texas, U.S.A.

Charles R. Herd
Operations and Technology Center, Columbian Chemicals Company, Swartz, Louisiana, U.S.A.

William M. Hess
Operations and Technology Center, Columbian Chemicals Company, Swartz, Louisiana, U.S.A.

Paul C. Julien
Webster Research Center, Xerox Corporation, Webster, New York, U.S.A.

Gerhard Kühner
Inorganic Chemical Products Division, Degussa AG, Frankfurt (Main), Germany.

Alain Le Méhauté
Département Matériaux et Procédés, Alcatel Alsthom Recherche, Marcoussis, France.

Nicolas Probst
Chemical Products Division, M. M. M., Brussels, Belgium.

Donald Rivin
Department of the Army, Natick Research, Development and Engineering Center, Natick, Massachusetts, U.S.A.

William L. Sifleet
Billerica Technical Center, Cabot Corporation, Billerica, Massachusetts, U.S.A.

Marcel Tommé
Billerica Technical Center, Cabot Corporation, Billerica, Massachusetts, U.S.A.

Claude Tricot
Département de Mathématique, Ecole Polytechnique, Montreal, Quebec, Canada.

Manfred Voll
Inorganic Chemical Products Division, Werk Kalcheuren, Degussa AG, Hürth, Germany.

Meng-Jiao Wang
Department of Applied Technology, Fillers and Rubber Chemicals, Inorganic Chemical Products Division, Degussa AG, Hürth, Germany.

Siegfried Wolff
Department of Applied Technology, Fillers and Rubber Chemicals, Inorganic Chemical Products Division, Degussa AG, Hürth, Germany.

INTRODUCTION

The term "carbon black" refers to a group of industrial products involving thermal, furnace, channel and acetylene blacks. They essentially consist of elemental carbon in the form of near spherical particles of colloidal size, coalesced into particle aggregates and agglomerates, and are obtained by the partial combustion or thermal decomposition of hydrocarbons. The use of carbon blacks dates back many centuries to when the Chinese and Indians used them as pigment in black ink in the third century B.C.

Carbon black is widely used as a filler in elastomers, plastics and paints to modify the mechanical, electrical and the optical properties of the materials in which they are dispersed and consequently determine their applications in a given market segment. Carbon black when compounded with plastics imparts unique properties such as UV protection, electrical conductance, range of darkness (jetness), opacity and reinforcement; when used in rubber these fillers change its fracture behaviour and improve abrasion and failure properties. About 90% of the worldwide production of carbon black is used by the tire industry where the carbon black enhances tear strength and improves modulus and wear characteristics of the tires.

Carbon black is an important pigment for use in xerographic toners as it plays a significant role in maintaining a suitable level of electric charge on the toner which is essential for proper operation of the electrographic copiers and printers. In 1992 in the USA alone, the copier industry consumed over 2000 metric tons of carbon black. This is relatively a small market compared to the industry. However, it is a significant portion of the market for speciality blacks.

The primary carbon black characteristics that influence the properties of carbon black compounds with elastomers are the particle size, aggregate size, the morphology of the carbon black aggregates and its microstructure. In addition, the nature of the carbon black surface and its characteristics with respect to its structural organization, porous structure, surface area and its chemical composition are of vital importance. A more precise knowledge of the chemistry of the carbon black surface is also essential for the proper development and improvement of carbon black for specific applications. The surface acidity and the dispersion properties of the various colour blacks have a great influence on thier performance in xerographic toners.

Carbon blacks are electrically conductive and impart good conductivity to thermoplastic polymers. Consequently they are used in the manufacture of conducting compounds. The electrical and dielectric behaviour of a polymer-carbon black compound depends upon the concentration, the nature and the characteristics of the carbon black, the nature and the molecular weight of the polymer and the mixing and finishing conditions.

Chapter 1

MANUFACTURE OF CARBON BLACK

Gerhard Kühner and Manfred Voll
Degussa AG,
Frankfurt (Main)/Hürth, Germany

Carbon black can be ranked as being one of the oldest manufactured products and its usage as a pigment for the production of India inks and mural paints can be traced back to the ancient Chinese and Egyptians. However, it was after the invention of movable type in the fifteenth century that the printed book became the most important means of communicating information, and as a consequence the demand for a strong black pigment increased steadily.

The most important event which was to have the greatest influence on the usage of carbon black occurred at the turn of the century and involved the discovery of the reinforcing effect of carbon blacks when added to natural rubber, a discovery that was destined to become the most significant milestone in the rubber and automotive industry. By using carbon black as a reinforcing filler the service life of a tire was greatly increased, ultimately making it possible to achieve durabilities of several ten thousand kilometers. Today carbon blacks play an important role, not only as a reinforcing filler for tires and other rubber goods but also as a pigment for printing inks, coatings, plastics, and a variety of other applications.

For several thousand years the use of carbon blacks was only possible after a suitable production process became available. It is a well-known fact that restricting the access of oxygen to the flames of burning oils or resins results in the formation of carbonaceous materials, an effect which was the basis of all historic production processes.

The majority of industrial carbon blacks produced today is also based on the process of "incomplete combustion" of hydrocarbons. However, a second process is also used, namely that of "thermal decomposition", during which the carbon black is formed in the absence of oxygen. These two process definitions may serve as a preliminary classification which subsequently will be subdivided further.

For the manufacture of industrial blacks the only processes used today are those which can be precisely controlled by appropriate measuring and control techniques, thus allowing the production of carbon blacks with clearly defined properties. They are therefore different from those processes in which soot is released as a contaminated byproduct, such as occurs in poorly adjusted heating ovens or during the uncontrolled burning of carbonaceous materials like wood, coal or oil. This chapter deals only with processes which yield clearly defined end products and for which the English term "carbon black" has been adopted in many countries.

1.1. THE CARBON BLACK INDUSTRY

As a member of the carbon family, carbon black differs from other carbon-based materials in many respects, an important one being that of bulk density. This property has prompted carbon black production facilities to be sited as close as possible to consumers since, when compared with carbon black feedstock, the transportation costs for carbon black are considerably higher. As a consequence carbon black plants are concentrated in those parts of the world where major portions of the industry requiring this material are located (Table 1).

The most important regions are North America, West and East Europe, and Asia, while South America, Africa, and Australia are at the lower end

Table 1. Distribution of World Carbon Black Production Capacity

Region	Number of plants	Estimated capacity, 1000 tons/year	Capacity share, %
North America	25	1925	27
West Europe	20	1420	20
East Europe	20	1485	21
Asia	69	1750	24
South America	8	410	6
Africa/Australia	4	165	2
World total	146	7155	100

of the scale. Today the global installed capacity is in excess of seven million tons per annum, with a worldwide demand for carbon blacks currently in the order of six million tons per annum. This quantity is produced by more than 140 carbon black plants situated in 35 countries.

Since carbon black is predominantly used as a rubber reinforcing material and mainly in tires, most of the carbon black production facilities are located in those countries possessing major tire and automotive industries.

Table 2 shows the 10 major carbon black producing countries. The "top ten" have each capacity of over 200,000 tons per annum, sharing together 77% of the total world capacity.

Following the rationalization and concentration of the automotive and tire industries, a consolidation of the carbon black industry also took place with the result that, of five major U.S.-based producers having worldwide activities in 1980 only two, Cabot and Columbian, survived – with the German-based company, Degussa, becoming a third major producer. These three companies operating globally, together with those local producers having capacities in excess of 200,000 tons per annum, are listed in Table 3.

This table shows that the seven major producers listed account for 57%

Table 2. Major Carbon Black Producing Countries

Country	Number of plants	Estimated capacity, 1000 tons/year	Capacity share, %
1. USA	20	1570	22
2. CIS[a]	20	1200	17
3. Japan	12	780	11
4. Germany	5	405	6
5. China	40	300	4
6. France	3	280	4
7. Brazil	3	255	4
8. South Korea	3	250	3
9. Italy	3	210	3
10. India	7	210	3
Total 1 - 10	116	5460	77
Other countries	30	1695	23
World total	146	7155	100

[a] *Commonwealth of Independent States (former USSR).*

Table 3. Major Carbon Black Producers

Country[a]	Number of plants	Estimated capacity, 1000 tons/year	Capacity share, %
1. Cabot/USA	26	1725	24
2. Degussa/Germany	10	830	12
3. Columbian/USA	10	595	8
Total global producers	46	3150	44
4. Huber/USA	3	270	4
5. Sid Richardson/USA	3	245	3
6. Tokai Carbon/Japan	3	230	3
7. Witco/USA	3	200	3
Total "Big Seven"	58	4095	57
Others	88	3060	43
World total	146	7155	100

[a] *Plants and their capacities are included if at least 50 % of the shares are controlled by the company.*

of the total world capacity with the three top global producers sharing between them 44%. The three companies - Cabot, Degussa, and Columbian - are not only the leading manufacturers of rubber grades but also of pigment and specialty blacks on a worldwide basis.

The rubber industry is by far the largest consumer of carbon blacks, accounting for approximately 90% of total carbon black sales, the major portion being concerned with sales to the tire industry. However, not only tires but also mechanical rubber goods and carbon black filled plastics are major component materials used in automotive production. Consequently, growth and development of the automotive industry, combined with changes in driving behavior, are key factors having the most significant influence on carbon black production.

The remaining 10% is sold to the non-rubber industry. Their uses as pigment blacks in printing inks and in the plastic industry are by far the most important. Both of these sectors are estimated as consuming roughly one-third each of total pigment black sales. The next important application, especially for the higher-priced, fine-particle-size blacks, is in the production of black paints and coatings taking about 9% of production. This is followed by the paper industry, consuming about 4%.

Table 4. Breakdown of Total Carbon Black Sales According to the Fields of Application (Estimated)

Rubber/non-rubber,	%	Non-rubber,	%
Tires	65		
MRG[a]	25		
Total Rubber	90		
Non-rubber	10	Printing inks	30
		Plastics	36
		Coatings	9
		Paper	4
		Others	21
		Total pigment	100
Total	100		

[a] *Mechanical rubber goods.*

Other areas, not based on the pigmentation characteristics of carbon blacks but which, nevertheless, are classified as applications for pigment blacks are manufacture of electrodes and reduction of metal oxides, etc. These applications altogether have a share of about 21% of total pigment black sales (Table 4).

The overall growth rate of carbon black production is between 1 and 2% per annum. This surprisingly low percentage, compared with the production records of the automotive industry, is due to the fact that the service life of tires has been continuously improving. The first major step in this field was made with the introduction of the so-called “improved blacks” which provided superior performance in treadwear at little or no extra cost. This development has been continued with the introduction of high-performance carbon blacks which are making a substantial contribution to continued performance improvement.

Additionally, the switch from bias to radial-belted tires was a major advancement in tire performance, significantly increasing the tire’s service life. These are the main reasons why overall sales of carbon black have more or less been in a state of stagnation for the last 15 years.

With detailed examination it is possible to highlight growth rates for the main sectors of application, and it can be seen that pigment grades show a more pronounced growth rate compared with that of rubber grades, particularly those used in tire production.

1.2. CARBON BLACK MANUFACTURING PROCESSES

Considered on a worldwide basis the average plant capacity is approximately about 50,000 tons per annum. In practice, however, the individual annual production capacities may vary between 15,000 and 150,000 tons. One plant usually comprises several production lines allowing different carbon black grades to be produced simultaneously. Such a carbon black plant having three production lines is shown in Fig. 1. This plant is located in the Netherlands, close to Rotterdam. Another one, with a capacity of more than 150,000 tons per annum is located in Germany, near Cologne (Fig. 2). The latter plant is the largest one in Europe and produces carbon black according to three different processes.

In principle a large-scale industrial plant for the production of carbon blacks consists of the following sections:

I. storage facilities for feedstocks,
II. carbon black production units,
III. equipment for the separation of carbon black from the process off-gas (tail gas),
IV. final processing of the carbon black,
V. storage facilities for the end product,
VI. utilization of waste gases.

The individual sections are interconnected by transport and conveying facilities which are completely closed systems in modern carbon black plants avoiding the release of carbon black dust into the surroundings. Industrial carbon blacks constitute no health hazard [32]. However because of its considerable coloring strength the product is regarded as a nuisance dust. Therefore, emission controls are an important aspect of carbon black production.

1.2.1. Classification of Carbon Black Manufacturing Processes

From a chemical point of view, it is essential to classify carbon black manufacturing processes into two categories of incomplete combustion and thermal decomposition of hydrocarbons, depending upon the presence or absence of oxygen [31]. The process of incomplete combustion, termed thermal-oxidative decomposition, is by far the most important one. In terms of quantity, the second process, i.e., the thermal decomposition of hydrocarbons in the absence of oxygen, plays only a very limited role.

The thermal-oxidative processes can be further subdivided according to certain flow criteria. The formation of carbon black in a turbulent flow is different from that in diffusion flames. An oil-fired domestic central heating boiler may serve as an example of a turbulent flame, whereas a well known example of a diffusion flame is a burning candle, at which we will take a closer look. The flame of a candle consists of several zones layered like skins of an onion. In the outer zone, where sufficient oxygen is available from the sur-

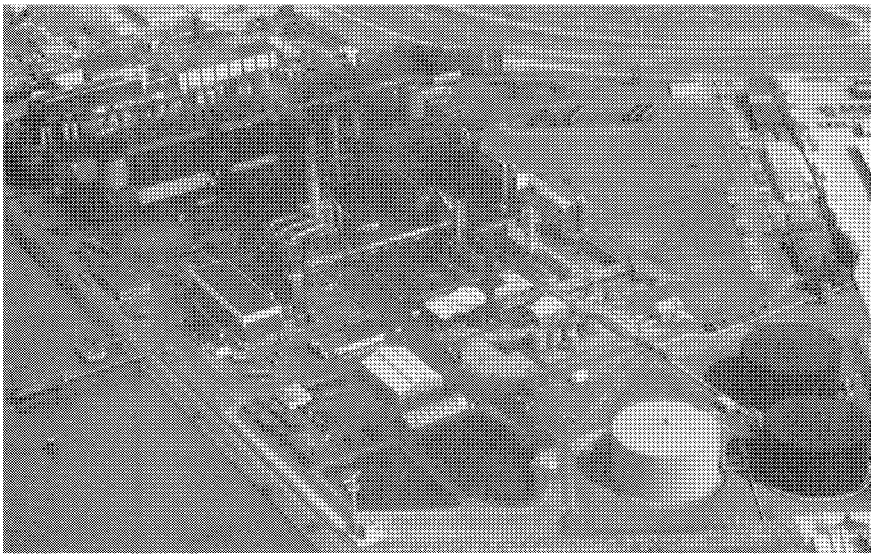


Fig. 1. Carbon Black Nederland B. V., Botlek, a Degussa AG affiliate.

Fig. 2. Carbon black plant, Degussa AG, Kalscheuren, Germany.

rounding air, the carbonaceous material burns almost completely. Simultaneously, heat is generated which melts and vaporizes the wax. The next inner zone is characterized by a deficiency of oxygen. Since the diffusion rate of oxygen is lower than the rate of the decomposition reaction, carbon is formed which causes the flame to glow. Normally, the decomposition products are burned as soon as they reach the outer zone containing sufficient oxygen, but if a cold object is held in the flame the reaction temperature will decrease and the combustion will be reduced to the extent that the carbon particles are no longer burned, but deposited on the surface of the cold object.

This process represents an open system, since oxygen from the surrounding air has free access to the diffusion flames and any lack of oxygen is only local and temporary. Carbon black formation in a turbulent-flow environment requires a closed system with an appropriately designed flow reactor. The advantages of a closed system are clearly apparent. The reaction components can be introduced in accurately controlled quantities and also independent of each other, giving the process considerable flexibility. In addition, a closed system prevents loss of carbon black from the production unit into the surroundings, avoiding unwelcome pollution.

In practice, the methods used to produce carbon black can be classified according to the above criteria as shown in Table 5.

As previously stated, the thermal-oxydative process is by far the most important for the production of carbon black and accounts for more than 98% of carbon black consumed worldwide. The reaction takes place at high

Table 5. Classification of Manufacturing Processes and Feedstocks

Chemical process	Production process	Feedstock
Thermal-oxidative decomposition		
Closed system (turbulent flow)	Furnace black process	Aromatic oils based on coal tar or crude oil, natural gas
	Lampblack process	Aromatic oils based on caol tar or crude oil
Open system (diffusion flames)	Degussa gas black process	Coal tar distillates
	(Channel black process[a])	Natural gas
Thermal decomposition		
Discontinuous	Thermal black process	Natural gas (oils)
Continuous	Acetylene black process	Acetylene

[a] *Historic.*

temperatures in a refractory-lined reactor or "furnace" – from which the term "furnace black process" is derived. The lampblack process also falls into the category of thermal-oxidative decomposition taking place in a closed system. Today carbon black production by this process is limited to one grade only. The processes constituting thermal-oxidation in open systems are the gas black process and the historic channel black process.

The thermal decomposition of hydrocarbons is carried out in closed systems, and two major processes belong to this category, namely those of thermal black and acetylene black. The thermal black process is cyclic, and the energy required to decompose the hydrocarbons is generated separately without production of any carbon black. In the acetylene black process, acetylene is decomposed in an exothermic reaction, permitting the process to become continuous once the reaction has been initiated.

1.2.2. Individual Sections of a Carbon Black Production Plant

The diagram in Fig. 3 shows the individual process steps in carbon black manufacture. The heart of the process is the carbon black production unit (1) which, depending on the process, may consist of reactor(s) or apparatus. The initial product of the unit is a mixture of process gas and carbon black suspended in the form of an aerosol. This aerosol is cooled and directed into collecting systems (2), where the solids are separated from the process gas. The carbon black thus obtained has a fluffy appearance, hence the designation "fluffy black". Due to its low bulk density and its tendency to dust, the black cannot be handled in this form and, therefore, must to be subjected to some form of densification (3-5). The fluffy black is either densified to powder black (5) or pelletized and, depending on the pelletizing process, dry- (4) or wet-pelletized (3) carbon black is obtained. The carbon black is then conveyed to the storage and packaging sections (6-7). Powder black is always packed in bags (8), whereas pelletized black is shipped either in bags, usually shrink- or stretch-wrapped on pallets (7-10), or as bulk or semibulk material (11) in road or rail tankers or in containers.

1.3. FEEDSTOCKS

As mentioned initially, hydrocarbons are the raw materials on which the production of all carbon blacks is based, and from the shape of the carbon black particles it can be concluded that they are formed in the gas phase. The carbon black particles and aggregates resemble those of other products obtained by pyrogenic processes, such as those found in fumed silica. One major prerequisite, therefore, is that the carbon black feedstock must be capable of being completely converted into the gaseous state. Consequently, the feedstocks used are either gases or liquids which can be vaporized under the given reaction conditions. In the case of the thermal-oxidative processes, non-vaporized hydrocarbon molecules can be broken into smaller fragments

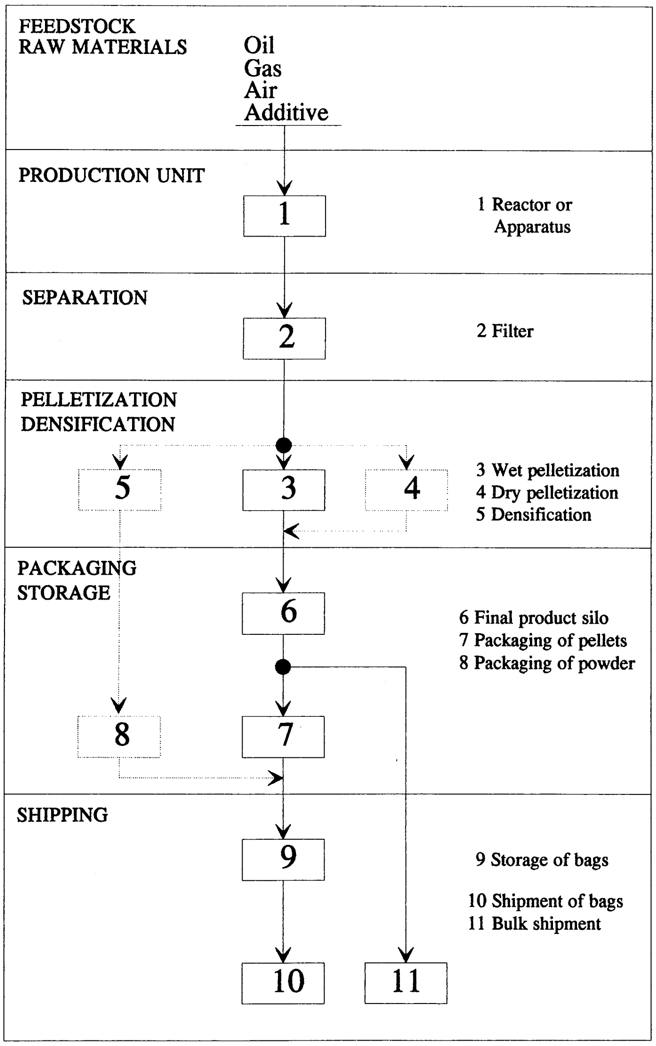


Fig. 3. Schematic diagram of the individual process steps in a carbon black production unit.

by the attack of oxygen, thus converting them into the gaseous phase. Larger polymeric hydrocarbons such as certain asphaltenes cause the carbon black to be contaminated with grit, i.e., products similar to coke, the particles of which are much coarser than carbon black and have a completely different shape.

On account of its availability, natural gas is the most frequently used raw material among the gaseous hydrocarbons. Only the acetylene black process constitutes a special case, since, as the name suggests, it uses only acetylene as the feedstock.

The preferred raw materials for other production processes of carbon black, besides natural gas, are oils which have a high content of aromatic hydrocarbons. Aromatics containing a number of condensed rings are particularly advantageous in terms of production yield, since the carbon/hydrogen ratio increases with the number of rings. The absence of side chains also improves the C/H ratio, and aromatics without them are therefore preferred. Since the feedstock has to be vaporized, the boiling point of feedstock oils must not be too high. More suitable feedstocks consist mainly of aromatics with three- or four-membered rings. Some important components of carbon black feedstocks are listed in Table 6.

In practice, both carbochemical and petrochemical oils are used as feedstock sources (Table 7).

Carbochemical oils are fractions obtained during coal tar distillation. Depending on the conditions of the distillation, coal tars contain up to 18% highly aromatic fractions which can be used as carbon black feedstocks. Besides other materials such as naphthalene and washing oils, electrode pitch is one of the main products obtained from tar. The sulfur content of these oils can vary between 0.5 and 0.7%, depending on the origin of the coal. The availability of carbochemical oils obtained from coal tar is largely dependent on the production of coke used in the manufacture of steel. The quantities available today are not sufficient to satisfy all the demand for carbon black feedstocks. Also, in highly industrialized countries, production of carbochemical oils is declining.

Although carbochemical oils are preferred in terms of efficiency, petrochemical oils are more important in terms of quantities available, particularly in the production of furnace blacks. These are residual oils resulting either from catalytic cracking processes (catcracker decant oils) or from the production of olefins in steam crackers using naphtha or gas oil as a raw material.

Table 6. Aromatic Hydrocarbons Contained in Carbon Black Feedstocks

Aromatic hydrocarbons	Formula	C/H-ratio, weight %	Carbon content, weight %	Factor, f_c[a]
Benzene	C_6H_6	11.9	92.3	1.08
Naphthalene	$C_{10}H_8$	14.9	93.7	1.07
Methyl naphthalene	$C_{11}H_{10}$	13.1	92.9	1.08
Dimethyl naphthalene	$C_{12}H_{12}$	11.9	92.3	1.08
Trimethyl naphthalene	$C_{13}H_{14}$	10.1	91.7	1.09
Anthracene	$C_{14}H_{10}$	16.7	94.3	1.06
Phenanthrene	$C_{14}H_{10}$	16.7	94.3	1.06
Pyrene	$C_{16}H_{10}$	19.1	95.0	1.05

[a] *Factor* f_c = *100/carbon content.*

Table 7. Processes Yielding Carbon Black Feedstocks

Type of feedstock	Raw material/Source	Manufacturing process
Carbochemical oils		
Coal tar oils	Unrefined coal tar	Distillation to obtain washing oils, electrode pitch and other valuable carbonaceous materials
Petrochemical oils		
Steam cracker oils	Naphtha, gas oil	Steam cracking to produce ethylene, propylene, and other olefins
Catcracker oils	Heavy petroleum fraction	Fluid catcracking processes to produce gasoline
Aromatic concentrates	Distillation residues from oil refineries	Extraction with furfural to obtain greases and lubricating oils
Mixed oils	Mixtures of different oils of various origins	

In Europe, mainly steam cracker oils are available, which can be low in sulfur content (< 0.2%), particularly, when naphtha is used as a raw material. In the United States, where catalytic cracking units are favored by the petroleum industry for production of gasoline, catcracker oils tend to predominate. These types of oils may contain up to 2.5% sulfur, sometimes even more.

The availability of aromatic concentrates extracted during the production of lubricating oils and greases is no longer significant these days.

It is apparent from the above that carbon black feedstocks are exclusively byproducts of processes used for the production of special chemical products such as electrode pitch, ethylene and gasoline [1]. Nevertheless, the choice of carbon black feedstocks is not merely determined by price and efficiency, but also by specific quality criteria. However, due to their origin, the feedstocks are mixtures of a large number of individual substances and are, therefore, not easy to characterize. More than 200 different components have been recorded in the range able to be detected by gas chromatography.

An important parameter for the evaluation of carbon black feedstocks is the density, since it increases with increasing aromaticity. It is also used for determination of the Bureau of Mines Correlation Index (BMCI) [2], which is obtained either from density and midboiling point or from density and viscosity for those feedstocks which cannot be distilled completely. This index is used by the carbon black industry as an important criterion for feedstock evaluation. An economically viable feedstock should have an index above 110. The BMCI and some other data describing the quality of the three most important types of carbon black feedstocks are listed in Table 8.

More detailed information than that provided by the density or the BMCI is obtained from distillation curves or gas chromatograms, which provide information concerning the chemical composition, the density, the boiling behavior and the C/H ratio of the feedstock. The C/H ratio can also be determined by elemental analysis which, in addition to carbon and hydrogen, gives the nitrogen, oxygen, and sulfur contents. The relevance of the C/H ratio is that it provides an indication of the aromaticity of the feedstock (Table 6). The aromaticity can be estimated more precisely by means of NMR spectroscopy by determining the ratio between aromatic and aliphatic C-H bonds, but this analysis is not performed on a routine basis.

Additional information can be gained from the distillation residue or from liquid chromatography. Asphaltenes, determined as pentane-insoluble matter, provide indications concerning the possibility of grit formation. Further analyses are carried out to determine the content of foreign elements such as halogens, alkali, alkaline earth and heavy metals. The alkali metals, in

Table 8. Data of Typical Feedstock Grades Produced by Different Processes

	Steamcracker process	Catcracker process	Coal tar distillation
BMCI	127	132	161
Density at 15°C, g/cm^3	1.07	1.101	1.136
API gravity at 15°C	n.a.	-3.04	n.a.
Viscosity, SSU at 100°C	120	82	80
Midboiling point, °C	n.a.	n.a.	355
Flash point, °C	70	130	90
Pour point, °C	30	30	60
Distillation residue, wt%	21.8	n.a.	2.7
Asphalthenes, wt%	19	8	1.65
Toluene insolubles, wt%	0.1	0.01	0.04
Water, wt%	0.1	0.1	0.1
Ash, wt%	0.02	0.05	0.04
Carbon content, wt%	92.0	90.6	92.1
Hydrogen content, wt%	7.11	7.05	6.4
C/H ratio, p.wt	12.9	12.9	14.3
Sulfur, wt%	0.2	2.1	0.6
Sodium, ppm	0.8	1.2	1.6
Potassium, ppm	0.3	0.1	0.2

particular, are subjected to tight specifications due to their influence on the structure formation of carbon blacks produced by the furnace black process. Oxygen in the feedstock has an adverse effect on yield and is therefore not desired. The sulfur content is restricted in many countries due to environmental laws limiting the emission of sulfur compounds in the waste gases. The viscosity, the pour point, and, for safety reasons, the flash point determine the handling properties and storage conditions of the feedstock. Specific details of carbon black feedstocks which are relevant for the manufacturing process will be discussed in corresponding sections which follow.

Until the mid-19th century, vegetable oils, fats, waxes and resins were used in the manufacture of carbon black, and in this class of products pine resin was of particular importance as a feedstock. With the onset of large-scale production of steel, which uses coke as a source of carbon, coal tar oils became available and were used in the production of lampblacks. In the U.S.A., natural gas has become the most important feedstock and was used in the production of channel and gas furnace blacks. However, emergence in 1941 of the oil furnace process led to a continuous shift towards petrochemical feedstocks.

1.4. PRODUCTION BY THE FURNACE BLACK PROCESS

The furnace black process is the most modern process for the manufacture of carbon black, and is particularly flexible and economical. By the criteria described above, this process uses the principle of oxidative decomposition. The process is continuous, and is operated in closed reactors where highly turbulent flows prevail due to high flow velocities. Because of its importance for large-scale industrial carbon black production this process will be described in detail. Except for the actual carbon black production unit, i.e., the furnace black reactor, other plant sections such as the conveying, filtering and pelletizing installations, are very similar to those used in other carbon black manufacturing processes. These will, therefore, be discussed in detail only in the section dealing with the furnace black process. Specific differences regarding other processes will be pointed out in the appropriate sections.

1.4.1. Description of the Process

Following the general flowsheet in Fig. 3, Fig. 4 provides a schematic illustration of a production unit for the industrial-scale manufacture of wet-pelletized carbon blacks by the furnace black process.

The carbon black feedstock is pumped from the storage tank to the reactor (1) via an oil preheater. Gas and preheated process air are also fed into the reactor. At a certain distance from the feedstock injection the thermal-oxidative reaction is arrested by injection of water, whereby the carbon black formed and the reactor off-gas are cooled. After further cooling in heat ex-

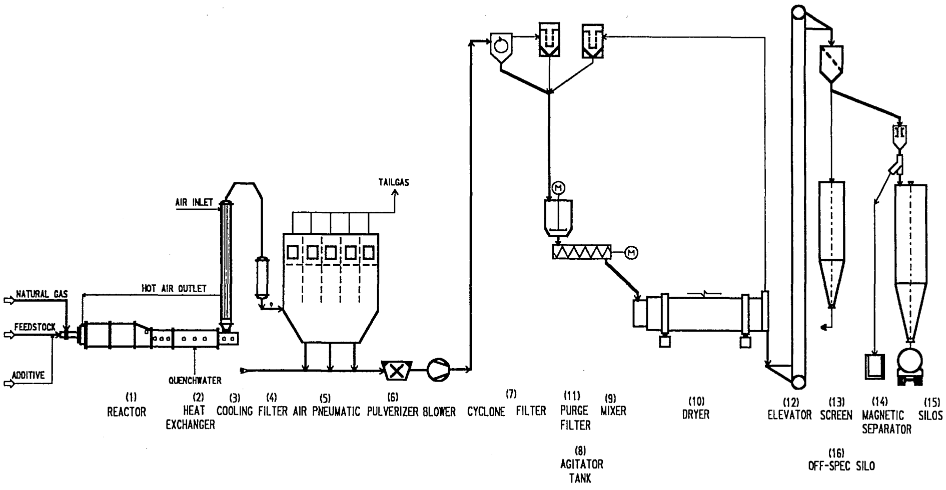


Fig. 4. Illustration of a furnace black plant.

changers (2,3), the mixture of carbon black and off-gas is directed into filters (4) where the carbon black is separated from the "tail gas". The filtered carbon black is then conveyed pneumatically (5) to the pelletizing section. Grit that may be present in the form of coarse particles is usually reduced to an acceptable size by the use of a hammer mill (6). After separation (7) and prior to the pelletizing unit, the carbon black enters a surge bin or agitator tank (8), which acts as a material buffer for the pelletizing unit and where some initial densification of the black takes place. Controlled amounts of black are then fed from the surge bin into a "pelletizer" or "pin mixer" (9) and mixed with approximately the same amount of water. The wet pellets formed are subsequently dried in a rotary kiln dryer (10) which is heated by hot gases preferably from the combustion of tail gas. Carbon black dust carried off by the dryer exhaust gases is collected in a filter (11) and recycled into the process. After leaving the dryer and before entering the storage silo, the carbon black pellets pass through screens (13) which act as classifiers for the pellet sizes, and through powerful magnetic separators (14) to remove any ferrous metal and rust contamination. The carbon black is conveyed to the storage silos (15) by means of bucket elevators (12), conveyer belts, and/or screw coveyors. From there it is discharged into the packaging units or directly to the bulk loading station. A separate storage facility serves as an "off-spec" silo and receives carbon black which does not meet the specifications. This may occur upon starting a production line or upon switching to a different grade. Depending on the type and extent of deviation, carefully controlled quantities of the "off-spec" black may be blended with material from subsequent production or eventually be used for applications not critical with respect to the quality deviation.

As previously mentioned, the tail gas is burned, and the generated heat is utilized in the dryers. Any excess gas can also be employed for generation of steam.

Fig. 5 depicts a plant for the production of furnace blacks.

This general survey of the manufacturing process is now followed by a description of the individual process steps.

Feedstocks and Additives

The necessary raw materials consist of gaseous or liquid hydrocarbons. For a better understanding of the process, one can differentiate between fuel and feedstock, although the limits between both materials are not clearly defined. Natural gas is the most frequently used fuel due to its ease of handling, whereas the feedstocks are comprised of the various types of oils described previously.

The distinction between fuel and feedstock is a simplification, since the two types of hydrocarbons cannot be varied independently. The ratio of the two materials depends on the carbon black's quality requirements and economic efficiency. Changes in the ratio between the natural gas fuel and the carbon black feedstock affect carbon black properties and are therefore

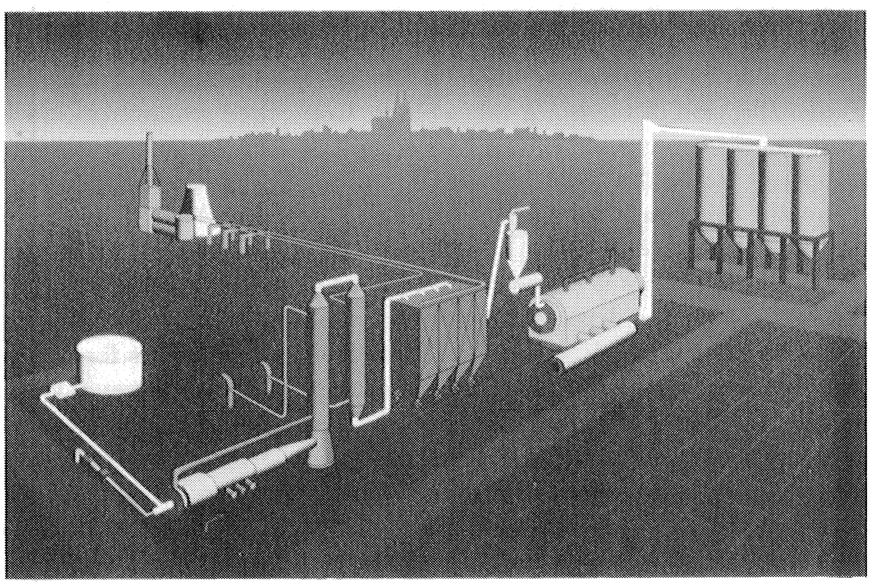


Fig. 5. Production plant for furnace blacks.

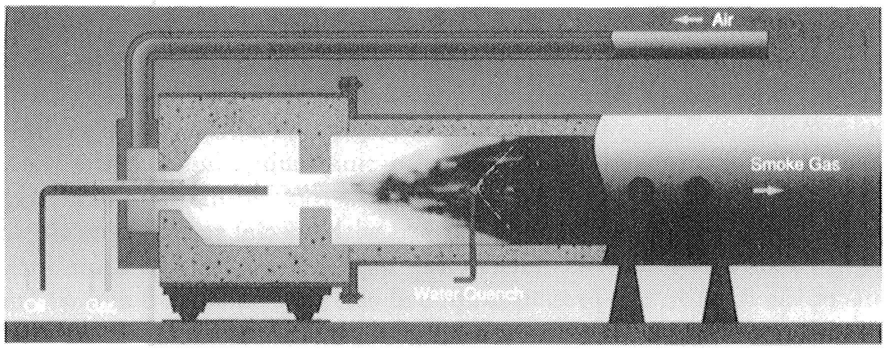


Fig. 6. Schematic representation of a furnace black reactor.

means of adjusting quality parameters (see *"Structure"*).
Fig. 6 provides a schematic representation of a furnace black reactor.

The first section of the reactor comprises of the combustion zone, where the fuel is burned in an excess of process air. In the subsequent section, the mixing zone, the carbon black feedstock is added and mixed as homogeneously as possible with the hot gases from the combustion chamber. In the third section, the reaction zone, a minor portion of the feedstock reacts with the remaining oxygen from the combustion chamber, but the major portion of the feedstock is pyrolyzed and decomposed into carbon black and off-gas. In the final section, the quench zone, the mixture resulting from this reaction is cooled by injection of water.

Although the most commonly used fuel is natural gas, propane or butane, synthetic gas or tail gas may also be used if natural gas is not available. If the calorific value of the gas is too low, the air may be enriched with oxygen in order to reach the required temperatures. Liquid fuels such as light or heavy fuel oils may also be used in place of gaseous fuels. In contrast to the carbon black feedstock, the requirement for fuels with respect to their chemical nature is simpler. In the case of commercial natural gas, the material is so inherently clean that no special requirements are needed. However, when, due to local conditions, the fuel is oil, some restrictions are necessary particularly with regard to sulfur content and trace elements. The decisive criteria of handling, air requirements and calorific values would apply for all fuel forms.

Carbon black feedstocks are usually stored in tanks capable of holding several thousand cubic meters of oil. Since most feedstocks are highly viscous at room temperature or may undergo partial crystallization, they are stored at elevated temperatures ranging from 70 to 120°C, depending on the feedstock type. The contents of the tanks are homogenized by stirring or by cycling. The feedstock oil is pumped from the storage tanks to the reactors either directly or via smaller day tanks which are used for intermediate storage and possible oil blending. The pipes are heated to maintain a desired viscosity and to prevent partial crystallization or solidification of the oil. In addition, the feed to the reactors is in the form of a ring main, thus keeping the oil in circulation even if none is fed into the reactor. Multistage centrifugal pumps are used. These pumps are equipped with special seals due to the low lubricating effect of these oils. Depending on the injection and atomization systems of the reactor, the pressures applied can vary between 8 and 40 bars.

Atmospheric air is commonly used as an oxidizing agent. If necessary the process air passes through a filter for cleaning, and is then compressed to approximately 1.5 bars by rotary-piston blowers, or onestage or multistage centrifugal blowers. Special reactor types are prepared to use oxygen-enriched air, partly in combination with higher pressures. Depending on the technique employed to atomize the oil, additional pressurized air or steam may be used to facilitate the atomization.

Alkali metal salt additives are employed to control carbon black "structure". The ions of these additives influence the degree of aggregation of primary particles in the flame [3]. Their effectiveness is solely determined by the cation of the alkali metal, a few ppm in relation to the carbon black feedstock, producing a considerable effect. Potassium salts are usually preferred which are commonly used in the form of aqueous solutions. Amounts of 10 – 2000 ppm of potassium in relation to the oil are applied, depending upon the extent of the desired reduction in structure and on the composition of feedstock used. To be effective, the salts have to be available in vaporized form during carbon black formation and hence are introduced either into the combustion chamber or together with the feedstock into the mixing zone.

To arrest the carbon black forming reactions and to avoid secondary reactions between the freshly formed carbon black and components of the reactor off-gas, water is injected into the reactor in the quench zone. This also acts to cool the mixture of carbon black and off-gas to a temperature suitable for the heat exchanger. Depending on the quality of the water available and the required purity of the carbon black, untreated, partially or totally deionized water can be used. In some cases, the total amount of quench water is split between a pre-quench and a main quench.

General Construction of Furnace Black Reactors

A feature common to all furnace black reactors is that they are enclosed in a gas-tight steel jacket. This is a major prerequisite permitting flows of all material to be closely controlled. This steel jacket is usually refractory-lined with highly heat-resistant material consisting of several layers of different types of ceramics. For the innermost layer, gas-tight material possessing the greatest heat resistance is used. It usually consists of alumina with very small amounts of silica, in order to improve the resistance against changes in temperature. Towards the outside are several layers having increasing silica contents and increasing porosity. This provides a gradually increasing insulating effect and a decreasing heat resistance. Instead of alumina/silica, chrome/aluminum oxides may also be used. Both materials provide refractory linings which allow reaction temperatures of up to, and sometimes above, 1900°C. When zirconia is used, the temperatures may even exceed 2000°C, but the use of this material is limited to oxidizing atmospheres found in the combustion chamber. The refractory lining may be constructed of bricks or from material which is cast and compacted. The use of bricks ensures the longest service life but is the most time-consuming and expensive method of producing shaped refractory sections. A relatively fast and easy way of preparing refractory linings, especially for intricately shaped reactors, is the use of material which is cast and compacted in situ. However, since the compaction is less than that of bricks and since it can only be sintered inside the reactor, cast refractories are less resistant to wear and have a shorter life cycle. Depending on the use of the reactor, the material employed and its location within the reactor, the life span of the refractory lining may be anything between a few months and several years.

The individual ceramic layers are chosen in such a way as to ensure that each layer offers the maximum insulating effect and the required heat resistance at the moment when the adjoining inner layer is at its maximum temperature. It is usually not possible to insulate the steel jacket, since a certain flow of heat is necessary to maintain the required temperature profile within the refractory lining. To avoid condensation, the outer steel jacket temperature should be approx. 130 to 150°C. If the lining is designed correctly, the heat loss from the reactor shell is in the order of 1 to 2% of the energy input. In special cases, when extremely high energy densities and temperatures are to be generated, particularly with oxygen enrichment, parts of the reactor may be provided with water cooling, sometimes without the refractory lining or with only a thin layer of refractory material.

Reactor geometries differ not only between the manufacturers (see Section 1.4.3), but are also dependent on the product range and the available fuels and feedstocks. In general, two main types of reactors are used to produce rubber-grade blacks. The reactors referred to as hard black or tread black reactors are used for the production of fine-particle carbon blacks of the ASTM 100, 200, and 300 series while those commonly referred to as soft black or carcass black reactors manufacture the coarser carbon blacks of the 500, 600, and 700 series. Carbon blacks having fine primary particles are obtained at higher reaction temperatures than the blacks with coarser particles. Hence the reaction is faster and the reactors are therefore designed for higher reaction velocities and shorter residence times. For the production of coarser carbon blacks, the reaction takes place at comparatively low temperatures and longer residence times are required, which can be accomplished in large volume reactors.

The functions of the individual elements of a furnace black reactor (Fig. 6), namely the combustion, mixing, reaction and quench zones, is now described in detail.

Energy is generated in the combustion chamber by reacting an oxidizing agent, usually air, sometimes enriched with oxygen, with the gaseous or liquid fuel. It is particularly important that air and fuel are mixed thoroughly, since the degree of the combustion and the volume of the combustion chamber are determined mainly by the mixing time. A complete conversion of the fuel into carbon dioxide and water in the combustion zone is required for optimum utilization of the energy input. High conversion rates are obtained by a thorough premixing of the fuel and process air, for instance by injecting the fuel transversely to the air stream at high pressure. By suitable choice of the size and number of gas nozzles, optimum premixing of the process air with the fuel is achieved at the location, where the gas is injected. Shear forces are utilized to achieve further mixing. They are generated by either injecting the gas transversely to the flow of air or by changing the cross section of the combustion chamber using chokes, venturis, restrictors or baffles. High flow velocities lead to increased turbulence and improve the combustion of the fuel. In some types of combustion chambers, the turbulence is further increased by creating a vortex in the flow, but care has to be exercised as this may cause a considerable back flow. All elements comprising the combustion chamber have to be carefully matched to obtain stable flames at the highest possible reaction rates. Modern combustion chambers allow energy densities of up to 100 MJ/m^3 to be achieved.

The process air is preheated by the waste heat generated by the process. Air temperatures of up to approximately 800°C are quite common. Compared to the stoichiometric air requirement of the fuel, the process air is usually in excess. This excess is necessary to limit the combustion temperature since the conventional refractory-lined combustion chambers are only able to withstand temperatures of up to 1900°C. In addition, the excess of air promotes the complete conversion of the fuel, especially at very high temperatures where the products carbon dioxide and water begin to undergo dissociation reactions.

The reaction in the combustion chamber is determined by the mass flows of process air and fuel, as well as by the process air temperature and the composition of the fuel. These are important parameters since they determine temperature, amount and composition of the gas leaving the combustion chamber. The fuel-to-air ratio is a key component and is best characterized by the air consumption factor. This consumption factor k, given in percent, defines the fraction of the total oxygen content of the process air consumed by complete combustion of the fuel. For gaseous fuel, k is given by:

$$k = 100 \times f_s \times gas/air \quad \% \tag{1}$$

where gas = fuel gas rate (Nm^3/h), air = the air rate (Nm^3/h) and f_s = the stoichiometric factor (Nm^3 air/Nm^3 gas).

In practice the air consumption factors lie between 30 and 80%. In refractory-lined combustion chambers, the air consumption factor has to remain below 80% when using high process air temperatures to avoid overheating, whereas air consumption factors below 30% are problematic due to reduced ignition velocity.

When different kinds of fuels are used, the air consumption factor is especially useful for comparing the states of the combustion zone and of the carbon black forming zone. The amount of gas leaving the combustion chamber, its temperature and composition, and especially the excess of oxygen can be easily calculated with this factor.

The energy input is estimated from the tangible heat introduced with the process air and the heat of combustion of the fuel. As a first approximation, the energy input H_i is:

$$H_i = 1.357 \times air \times T_{air} + gas \times H_u \tag{2}$$

where T_{air} = process air temperature (°C) and H_u = net heat of combustion of the gas (kJ/Nm^3).

Fig. 7 shows the temperature of the gas leaving the combustion chamber as a function of the air consumption factor and the air temperature, and it is apparent from the diagram that temperatures may easily exceed 2000°C. Since the upper limit for the commonly used alumina ceramic is 1900°C, unless special precautions are taken to dissipate the heat, the process air temperature and air consumption factor have to be adjusted.

As indicated above, the type of fuel may also vary. As long as the fuel contains only aliphatic hydrocarbons, there is a good correlation between the net heat of combustion of the hydrocarbons and the stoichiometric air requirement, as shown in Table 9. This relation is given by a regression analysis (r = 0.9999):

$$H_u = 4085 \times f_s - 3567 \tag{3}$$

where H_u = net heat of combustion of the fuel (kJ/Nm^3). Combining Equations 1, 2 and 3 allows the calculation of the energy input into the combustion chamber for any given fuel:

$$H_i = (1.357 \times T_{air} + 40.85 \times k - 35.67 \times k/f_s) \times air \tag{4}$$

In the mixing zone, the feedstock is introduced into the hot gases leaving the combustion chamber. This area is characterized by high shear forces

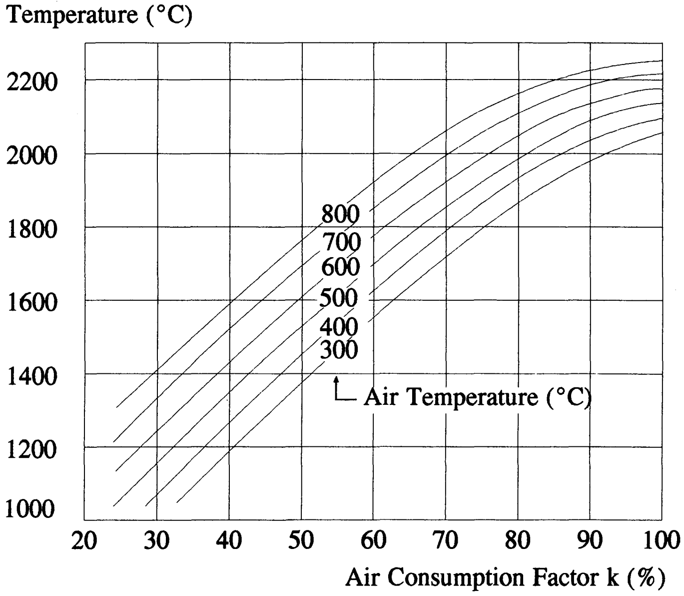


Fig. 7. Temperature of gases leaving the combustion chamber as a function of the air consumption factor and air temperature.

created by varying crosssections and high turbulences due to very high flow velocities, both of which can be increased by the action of a vortex. Gas velocities of 0.3 to 0.8 Mach are typical for most modern reactors. The carbon black feedstock is injected into the highly turbulent gases usually through nozzles designed to achieve optimum atomization and distribution in the flowing gases. Both single- and bi-fluid nozzles are in use. Bi-fluid nozzles have the advantage of providing better atomization in terms of smaller mean droplet sizes and are more flexible with respect to variations in throughput and atomizing energy. The disadvantage is that additional energy in the form of an atomizing medium is required, usually pressurized air or steam. The

Table 9. Stoichiometric Air Consumption and Net Heat of Combustion of Hydrocarbons

Hydrocarbons	H/C ratio	Stoichiometric air consumption, f_s, Nm³/Nm³	Net heat of combustion, H_u, kJ/Nm³
CH_4	4.0	9.55	35797
C_2H_6	3.0	16.71	64351
C_3H_8	2.7	23.87	93575
C_4H_{10}	2.5	31.03	123552

use of air entails the danger of coke formation at nozzles, whereas steam may adversely affect the yield due to partial gasification of the feedstock. Good atomization is achieved at gas pressures of 6 bar to 8 bars and gas loads of approximately 100 Nm^3/t of feedstock. Single-fluid nozzles are operated at pressures ranging from 6 bar to 40 bars. However, there are also other reactors in which the carbon black feedstock is not atomized but injected directly into the mixing zone in the form of coherent streams. In this case the atomization is obtained mainly by the shear forces of the gas stream. Consequently, such reactors require very high gas velocities (up to 1 Mach).

The throughput of a reactor is usually determined by the cross section of the mixing zone since the process air representing the largest volume determines the pressure drop in the reactor. Modern industrial scale reactors have production capacities of up to 4 t/h of carbon black. In principle it is possible to build even larger reactors, but this would not be economical. Due to production volumes in terms of carbon black output of large reactors the individual production runs would become too short.

The mixing zone is the most sensitive part of a furnace black reactor since its geometry has immediate consequences on the properties of the carbon black. There is a large variety of possible configurations (see Section 1.4.3). A glance at the various locations of feedstock injection shows that in some reactors the oil is injected through centrally located axial sprays, while some other reactors use sprays which are directed radially inwards. There are others which have a combination of both axial and radial sprays. The carbon black feedstock can be introduced downstream or upstream of, or directly at the site of highest flow velocity, or at a combination of these sites simultaneously. Any of the above-mentioned different nozzle types may be used at the various locations. Finally, there are different designs for the mixing zone in which its inlet and outlet may be either conical or stepped.

In the reaction zone which follows the mixing zone, the atomization and vaporization of carbon black feedstock is completed. The gas leaving the combustion chamber still contains some oxygen which reacts with part of the feedstock vapor. The temperature in the reaction zone is of particular importance, since it is largely responsible for the primary particle size of the carbon black. In refractory-lined reactors, the maximum temperature and thus the fineness of the particles are limited by the temperature resistance of the refractory material.

It is important for the production of carbon blacks that the feedstock is completely vaporized before the onset of pyrolysis, since carbon black can only be formed by the decomposition of hydrocarbons which are in a gaseous phase. If, due to process parameters or feedstock properties, droplets of oil are decomposed before they have been vaporized, spherical coke particles are formed which contaminate the final product. Coke grit can also be formed when liquid feedstock impinges upon the reactor walls.

The size of the reaction zone is mainly dependent on the throughput and the residence time required for the carbon black formation to be completed. To obtain the desired flexibility by controlling the residence time, the size of the reaction zone is not rigidly fixed, but must be capable of being adjusted depending on the carbon black grade which has to be produced. This is achieved by varying the positions along the reaction zone where the reaction mixture can be quenched by the injection of water. In this quench zone all major reactions are arrested or slowed down to such an extent that no further measurable conversion can take place.

One single quench may be sufficient and may serve as well to arrest the reaction as to adjust the reactor outlet temperature. However, several quench positions may also be used, one upstream to arrest the reaction and one downstream to control the reactor outlet temperature. Conventional atomizing nozzles with different spray characteristics (hollow- and full-cone nozzles, flat sprays) are used for the injection of water. Both axial co- or contra-flow or radial configurations are possible. Apart from the choice between different quench positions, the type and number of nozzle positions as well as the amount of water injected by the different nozzles offer additional means of a fine adjustment of quality parameters. If two quench positions are used, the quench temperature usually ranges from 900 to 1200°C, while the reactor outlet temperatures lie between 700 and 1000°C depending on the type and materials of construction of the heat exchanger.

During the process by which carbon black is manufactured different gases are produced, the composition of which depends on the stage of the process involved. Therefore, for correct understanding it should be appropriate to give a nomenclature to identify each of the gases.

There are four basic off-gases:

I. The combustion off-gas is the gas leaving the combustion chamber and becomes mixed with the feedstock before entering the reaction zone.

II. The reactor off-gas or smoke gas is the gas formed after the conversion of the feedstock into carbon black which acts as the gas carrier for the fluffy black entering the separation zone such as filtration.

III. The tail gas is the gas remaining after the filtration of the black and which, due to its calorific value, is used to produce heat for dryers in the wet pellet process, and for the steam boiler.

IV. The waste gas, as its name suggests, is the final product after all the combustibles have been burned and used for drying, power generation, etc.

Heat Exchanger

The reactor connects directly to a heat exchanger in which the reactor off-gas containing the carbon black is cooled and the process air is preheated. It is usually constructed as a tubular heat exchanger through which the process air passes in counterflow to the reactor off-gas. The reactor off-gas with the carbon black passes through a bundle of tubes which, depending on the size of the installation, may consist of between 50 and 200 tubes with diameters of 50 to 100 mm. The flow velocities are sufficiently high to prevent the carbon black from being deposited on the heat exchanger walls. In addition, special cleaning systems are employed to remove such deposits and to prevent plugging.

With reactor off-gas temperature between 700 and 1000°C at the inlet of the heat exchanger, and 400 to 600°C at the outlet, process air temperatures range between 400 and 800°C, with the most common air temperature lying between 600 and 750°C. Higher preheat temperatures are possible, but they would require the heat exchanger to be constructed from specialized and usually very expensive materials. In terms of energy, it would seem appropriate to always achieve the highest possible air preheat temperature. However, this is not always possible due to the temperature limitations of the combustion chamber, the possibility of fowling in the heat exchanger, and restrictions with respect to carbon black properties.

The mixture of carbon black and reactor off-gas leaving the heat exchanger at a temperature of at least 400°C has to be further cooled to 260-280°C before it may enter the carbon black separation units. This may be achieved by a second heat exchanger in the form of air or feedstock preheater, a waste heat boiler, or simply by the injection of water. With the second heat exchanger, also of a tubular type, air may be preheated for use in other processes. The steam obtained from a waste heat boiler may be utilized to preheat the feedstock or for other heating purposes. If the installation has an integrated oil preheater, additional cooling by injection of water is necessary.

Separation

The carbon black is separated from the tail gas by means of bag filters. Two different filter systems are in use, repress bag filters and pulse-jet filters. In repress-type filters, the deposited carbon black is removed from the filter bags in sequence by repressurization with filtered tail gas. Typical filter loads are in the range of 0.2-0.4 $m^3m^{-2}min^{-1}$. In pulse-jet filters, pulses of pressurized air or steam are applied to clean the filters bags. The advantage of pulse-jet filters is the higher specific load of the filter surfaces, so that compared to the repress type, these filters may be built smaller for the same filter capacity. A disadvantage is the greater mechanical strain on the filter bags. If air is used as a cleaning medium, the amount of air has to be limited so as to prevent the formation of flammable mixtures with the combustible tail gas. In all types of carbon black filters the carbon black is discharged from the filter bags into the filter cone or hopper, from which it is conveyed by means of a screw conveyor and rotary star valves.

In the past, the carbon black was separated from the tail gas by means of cyclones. Today, cyclones are only used infrequently as pre-separators or as agglomeration cyclones where a large part of the carbon black is first separated and then taken up again by the tail gas. The purpose of this technique is to achieve a limited agglomeration of the carbon black and thus facilitate the ensuing separation in the filters.

The filter inlet temperatures are in the range of 260 to 280°C, these comparatively high inlet temperatures being necessary to prevent condensation. Since the tail gas contains approximately 30-40% water, the dew point lies at least in the range of 70-80°C. The actual dew point may be much higher, depending on the sulfur content of the tail gases. In addition, the temperature of the walls of the filter housing may be far lower than that of the gas in the filter due to the excellent insulating capacity of the carbon black which becomes deposited on the filter walls.

The filter bags are usually made of special surface-treated glass fiber cloth. The service life of these filters may be up to two years depending on operating conditions and the sulfur content of the feedstock. The residual carbon black content of the purified tail gas varies slightly according to the carbon black grade. Values of 10 to 20 mg/m^3 can be achieved.

Due to the presence of combustible substances such as hydrogen, carbon monoxide, and some low molecular weight hydrocarbons, the filtered tail gas in most cases is utilized to generate heat for drying of the carbon black (see *"Densification and Pelletization"*) and for generation of steam. Some of the steam is consumed internally, but the largest part can be sold or used to generate electricity. A modern carbon black plant is capable of generating approximately three times the amount of electricity it consumes, the excess usually being sold to the local distribution network.

Conveying (Loose Black)

The carbon black discharged from the filter is conveyed pneumatically to other sections for further processing. Conventionally, tail gas or air are used as carriers. Both systems have their advantages and disadvantages. In the case of tail gas, it is less important that the seals at the discharge of the filters are absolutely gas-tight. Furthermore, since the tail gas is recirculated into the main filter, additional filters are not required. On the other hand, the high dew point necessitates higher temperatures than in the case of air, and corrosion may be a major problem. A considerable advantage when using air as a carrier is the fact that flammable gas is prevented from entering the pelletizing section. Any reaction between the freshly produced carbon black and air occurs already in the pneumatic system. Pneumatic systems for conveying powder blacks are usually operated at elevated temperatures, with conveying rates of 15-20 m/sec.

The carbon black is normally separated from the pneumatic system by means of cyclones which, in the case of an open air pneumatic system, are followed by a filter for cleaning. In the case of pneumatic systems using tail gas, the filter can be omitted since the tail gas is recirculated back into the process filter.

Purification

The carbon black may contain small amounts of solid contaminants such as coke particles, abraded particles from the refractory lining of the furnace or rust particles. These have to be removed prior to further processing. In many cases, it is sufficient to reduce such contaminants to acceptable particle sizes in micropulverizers.

Magnetic contaminations in the form of rust or metal abrasions can be removed by magnetic separators. The most simple method is to insert rod-shaped permanent magnets into the carbon black conveying pipe. They are taken out from time to time and cleaned. More sophisticated systems use electromagnets which are cleaned automatically at fixed intervals. However, in order to minimize the possibility of rust formation, most carbon black plants are increasingly using stainless steel and other corrosion resistant metals.

The most efficient elimination of solid contaminants is achieved by the use of grit separators. A simple variant is the gravity separator in which the carbon black and contaminants are separated by their different fall velocities. Better results are obtained with centrifugal separators, but these are technically more complicated and more expensive. They use rotors to generate high centrifugal forces. The separator conditions can be varied over a wide range by adjusting the rotor speed and the amount of auxiliary air.

Densification and Pelletization

The "fluffy" black separated from the pneumatic system still contains considerable amounts of air or gas and has a very low bulk density. Therefore it has to be further densified before it can be used commercially. The extent and the means of densification depend on the intended use of the carbon black.

An initial densification is achieved in the loose black surge bin, where the black is stirred slowly. The loose black surge bin is, therefore, also termed agitator tank. It not only ensures the initial densification of the black, but also acts as a buffer. Sensors allow its product level to be monitored and kept at a constant level so as to maintain a certain flow of carbon black through the screw conveyors or rotary star valves into subsequent densification processes.

The most controlled form of densification of the powder black is vacuum densification. It is achieved by passing the carbon black over porous rollers, the insides of which are under vacuum. The effect can be enhanced by gently pressing the carbon black against the vacuum roller by means of a second roller. This form of densification is adopted mainly for pigment blacks which are used in the powder form and must be very easy to disperse. It is self-evident that such blacks require special care during packaging, storage and transport to avoid any further densification.

Higher densification of the carbon black is achieved by pelletization. It is the preferred method, if the application system and mixing equipment of the customer develops high shear forces for a more intensive dispersion of the black into the active media. With few exceptions, rubber-grade blacks are always pelletized, since only in this form can they be handled and incorporated into the various polymers using standard industrial equipment. Other advantages of pelletized blacks are smaller transport volumes, more favorable free-flow properties, and reduced dusting.

Because of their different characteristics it is necessary to differentiate between the two pelletizing methods commonly used, namely wet pelletization and dry pelletization. The process of dry pelletization makes use of the fact that densified carbon black particles can be formed into small round pellets in a rotating drum (dry mill). This process is continuous, but limited in its application. The higher the carbon black "structure", the more difficult is dry pelletization. In order to achieve the desired throughput, a certain proportion of pelletized carbon black is recycled to act as "seeds" for new pellets.

In the wet pelletization process, the carbon black is mixed with water in special pin mixers, in which the amount of carbon black and water has to be closely monitored. The pelletizer, or pin mixer, is a cylinder which is 0.5 to 0.7 m in diameter and approximately 3 m long. It has a rotating shaft along its axis on which are fitted steel pins in the form of a helix, the pins extending almost to the cylinder wall. The shaft rotates at 300-700 rpm and the pelletization water is injected towards the mixer axis through nozzles situated at different locations along the pelletizer. The water/carbon black ratio used is approximately 1:1 for most blacks. By the mechanical action of the pins wet pellets with a diameter of 0.5–2.0 mm are formed. If necessary, pelletizing agents or binders, such as molasses, lignin sulfonates, or sugar are added to influence pellet hardness. In principle, wet pelletization can be performed on all carbon black grades, but is rarely used in the case of pigment blacks because the densification is too high.

Since the ratio between carbon black and pelletizing water affects the pellet size, the degree of densification and hence the DBP number of the pelletized black, it is particularly important that this ratio is kept constant. Modern pelletizers are therefore fitted with a control device which uses the power demand of the mixer motor drive to keep this ratio constant since this power demand is very sensitive to the carbon-black-to-water ratio.

After leaving the pelletizer, the wet pellets have to be dried. This is achieved by rotary-kiln dryers heated externally, which may also be supplemented by hot gases passing through the dryer. Dryers with a throughput of 2–4 t/h have a diameter of 2–3 m and a length of 15–20 m. They rotate at a rate of about 6 rpm. Heat transfer and the motion of the carbon black may be improved by fitting additional components such as lifters in the dryer.

The bed depth of wet pellets and thus the residence time in the dryer can be varied by means of adjustable weirs. The dryer outlet temperature of the carbon black is 150–250°C. Since a certain oxidation of the carbon black surface may already occur at this temperature, selected carbon black properties which may be relevant to later applications can be influenced in this process stage by changing the bed depth and the temperature in the dryer. It is therefore important that the required temperature profile in the dryer is carefully controlled. This, however, can only be achieved with specific control devices. A problem may arise if the temperature of carbon black is too high when leaving the dryer. Due to its insulating property, its temperature will decrease slowly, and the carbon black may be too hot for loading and delivery to the consumer.

A special variant of carbon black pelletization is oil pelletization. It can be performed both as a dry or wet pelletizing process. During pelletization, 1–10 % of oil is added to the carbon black which wets the carbon black surface, facilitating dispersion in later applications.

Storage and Packaging

Powder Black: The densified fluffy black is collected in a silo from which it is transported to turbo or screw packing machines that are automated and make use of appropriate robotics to eliminate the former manual operations. The level of the product in the silo is kept low to prevent additional uncontrolled densification. Most carbon blacks are packed in multilayered paper sacks, but polyethylene bags are also used for products which are sensitive to moisture. The bags are stacked on pallets and shipped as such. In the case of powdered blacks the pallets may not be stacked.

Pelletized Black: From the pelletizing section, the pelletized black is transported by bucket elevators, conveyor belts and screw conveyors to single- or multiple-compartment storage silos with capacities between 100 and 1000 t. The pelletized black is stored in these silos from where it is discharged directly into road or rail tankers, intermediate bulk containers, or into automatic packaging lines.

The majority of rubber-grade blacks in Europe is shipped by road and through some rail tankers with a capacity of about 20 and 45 tons, respectively. In the U.S.A., rail tankers are preferred. Some carbon black is also packed and shipped in big bags of 500 or 1000 kg capacities. Smaller sacks containing 15-30 kg are packaged by automated high-speed packaging lines and stacked on pallets ready for shipment.

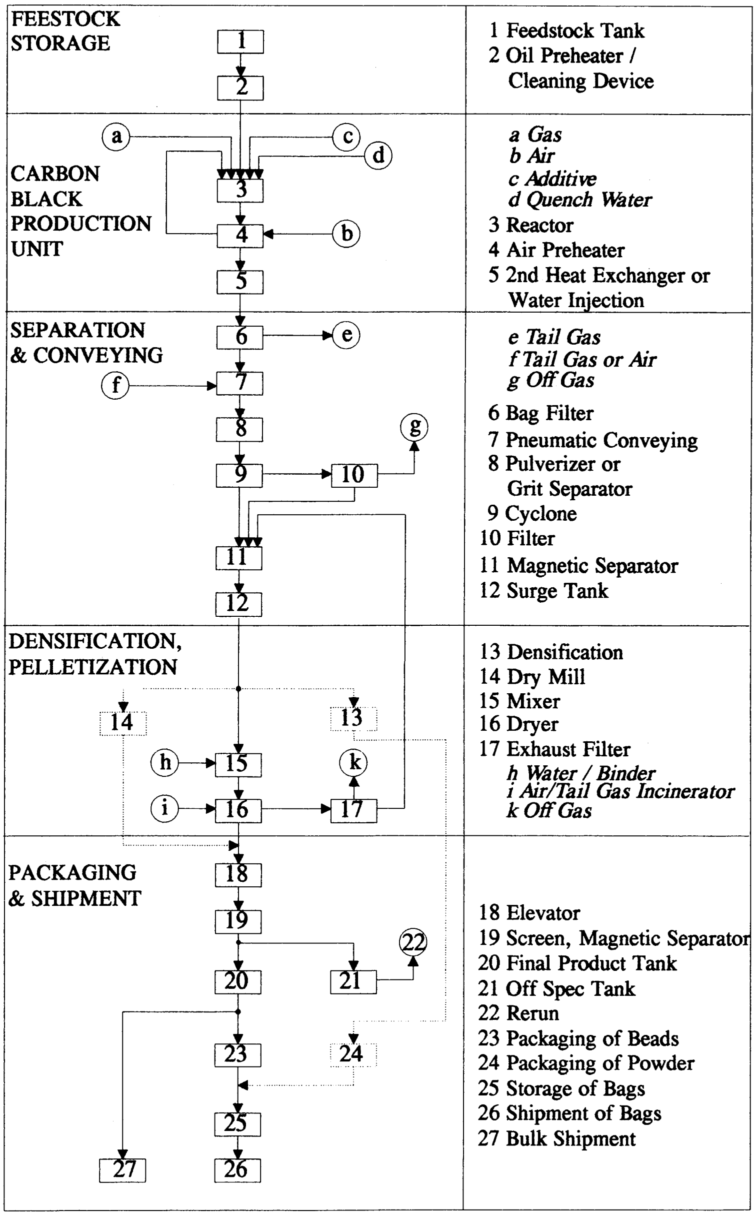


Fig. 8. Schematic illustration of a furnace black plant including the alternatives of powder blacks (13/24), dry pelletized blacks (14), and wet pelletized blacks (15/16).

Summary

In contrast to Fig. 3, Fig. 8 shows a much more detailed illustration of the individual process steps involved in a furnace black production unit.