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Edited by Jorge Ancheyta

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Jorge Ancheyta
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Mexico

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Contents

About the Editor

Jorge Ancheyta, PhD, graduated with a Bachelor's degree in petrochemical engineering (1989), a Master's degree in chemical engineering (1993), and a Master's degree in administration, planning and economics of hydrocarbons (1997) from the National Polytechnic Institute of Mexico. He splits his PhD between the Metropolitan Autonomous University of Mexico and Imperial College London, UK (1998), and was awarded a postdoctoral fellowship in the Laboratory of Catalytic Process Engineering of the CPE-CNRS in Lyon, France (1999). He has also been visiting professor at the Laboratoire de Catalyse et Spectrochimie, Université de Caen, France (2008, 2009, 2010), Imperial College London, UK (2009), and the Mining University at Saint Petersburg, Russia (2016, 2017).

Dr. Ancheyta has worked for the Mexican Institute of Petroleum (IMP) since 1989 and his present position is Manager of Products for the Transformation of Crude Oil. He has also worked as professor at the undergraduate and postgraduate levels for the School of Chemical Engineering and Extractive Industries at the National Polytechnic Institute of Mexico since 1992 and for the IMP postgrade since 2003. He has been supervisor of more than 120 BSc, MSc, and PhD theses. Dr. Ancheyta has also been supervisor of a number of postdoctoral and sabbatical year professors.

Dr. Ancheyta works on the development and application of petroleum refining catalysts, kinetic and reactor models, and process technologies mainly in catalytic cracking, catalytic reforming, middle distillate hydrotreating, and heavy oils upgrading. He is author and co-author of a number of patents, books, and about 250 scientific papers (H-index of 45), has been awarded the highest distinction (Level III) as National Researcher by the

Mexican government and is a member of the Mexican Academy of Science. He is Principal Associate Editor of the international journal *FUEL*. Dr. Ancheyta has also chaired numerous yearly international conferences since 2004, namely the International Symposium on Hydroprocessing of Oil Fractions and the International-Mexican Congress on Chemical Reaction Engineering.

Notes on Contributors

All the contributors have worked for the Mexican Institute of Petroleum (IMP, Instituto Mexicano del Petróleo) in the management of products for the transformation of crude oil in the direction of product technology. They have worked together since 1999 in the upgrading of heavy oils group. Throughout this time, the team has gained vast experience and worldwide recognition in the development of processes, catalysts, kinetic, and reactor models, particularly for catalytic hydrotreating of petroleum distillates, conversion of residue, upgrading of heavy oils, and production of clean fuels. The individual experience of each researcher is reflected in each of the chapters with the aim of guiding new and current scientists towards new developments in the fascinating world of petroleum refining. We would like to thank the many people from IMP and BSc, MSc, and PhD students who during this time have helped with experimental work, characterization studies, development of methodologies, and modeling work studies.

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Preface

Catalytic hydrotreating (HDT) is a mature technology that has been practiced in the petroleum refining industry for the upgrading of hydrocarbon streams for the last 60 years. For conventional distillate hydrotreating, the main purpose of the process is to remove impurities such as heteroatoms (sulfur, nitrogen, and oxygen) and saturate aromatic and olefinic compounds, whereas in the case of heavy oils and residues, it also comprises the elimination of metals (nickel and vanadium), conversion of asphaltene molecules, and hydrocracking of heavy fractions. Its major applications in current refinery operations can be grouped in the following categories: (i) feed pretreatment for conversion processes such as catalytic reforming, catalytic cracking, and hydrocracking, (ii) post-hydrotreating of distillates, and more recently (iii) upgrading of heavy crude oils. In the first case, generally the objective is to reduce the amount of sulfur, basic nitrogen compounds, metals and polynuclear aromatics, which act as deactivation agents in acid-catalyzed processes. The second category includes the finishing step to produce transportation fuels that meet ecological standards (e.g. ultra-low sulfur gasoline and diesel). The final group aim to increase the API gravity of the crude oil, reducing viscosity, removing impurities, and producing lighter and better quality oils.

There are numerous hydrotreating processes for handling all types of refinery streams and for each specific objective. They differ in reactor technology, catalyst type, operating conditions, and process configuration. Among all the reactor technologies, fixed-bed reactors are still the most widely used in HDT operations due to their flexibility and relative simplicity. Other types of reactors, such as moving-bed, ebullated-bed, and slurry-phase, are also available for upgrading the heaviest fractions.

Hydrotreating is carried out in a wide range of operating conditions. The severity of the process is adjusted depending on the properties of the feed and required product composition. The main process variables are pressure, temperature, hydrogen-to-oil ratio, and space-velocity. Each variable influences every single aspect of the process; therefore the set of operating conditions must be carefully tailored to achieve efficient operation.

For proper design of HDT processes and catalysts, experimental studies in different reaction scales are mandatory. The scaling-up steps must be carried out with great care based on appropriate experimental methodologies to ensure that the development of the process or catalyst will successfully end up in commercial application. To do this, as well as such methodologies, adequate experimental facilities for conducting characterization of hydrocarbons and catalysts, as well as for evaluating catalyst performance, are necessary.

Experimental Methods for Evaluation of Hydrotreating Catalysts provides a detailed description of experiments in different reaction scales that are typically used when studying processes and catalysts for hydrotreating different petroleum distillates. The book is organized into ten chapters:

- Chapter 1 introduces general aspects of the experimental setups used for conducting research studies for hydrotreating, such as type of operation, selection of reactor, experimental considerations, and analysis of products.
- Chapter 2 deals with experimentation in glass reactors with model compounds. The different parts of a glass unit are described, such as the microreactor, gas flow section, feed section, and product analysis. Details of calculations of molar concentration, partial pressure, reaction rate, and conversion are given. Step-by-step procedures for catalyst testing are also provided.
- Chapter 3 is devoted to experimentation with model molecules in batch reactors. The methodology for carrying out experiments in batch reactors is described in detail, and important reaction issues are highlighted, such as mass transfer effects, catalyst particle size, and kinetic studies.
- Chapter 4 describes experimentation in batch reactors with petroleum distillates. The use of batch reactors and modes of operation are discussed, as well as data collection and analysis of experimental data. Determination of catalyst effectiveness factor, reaction rate coefficients, and activation energy are also covered.
- Chapter 5 focuses on experimentation with heavy oil in a batch reactor. Apart from providing details of the experimental setup and procedures, examples of the preparation of supports and catalysts, and their use in the hydrotreating reaction are described. Advantages and disadvantages of batch reactors are also highlighted.
- Chapter 6 describes experimentation in small-scale continuous fixed-bed tubular reactors. Explanation of the experimental unit as well as catalyst loading, activation, unloading, and characterization are given. Tests with a series of different catalysts are discussed in terms of effect of diluent composition, catalyst support, support modification, and additive incorporation.
- Chapter 7 deals with experimentation in medium-scale continuous fixed-bed tubular reactors. Experiments for studying the isothermality of the reactor, flow regime, ideality of flow pattern, and mass transfer gradients are discussed. Examples of the use of the unit for hydrotreating heavy oil and middle distillates with different catalysts are given.
- Chapter 8 is devoted to experimentation in large-scale continuous fixed-bed tubular reactors. Different case studies are presented, such as hydrotreating of heavy residue, hydrotreating of highly aromatic petroleum distillates, characterization of spent catalyst from residue hydrotreating, and reaction kinetics for hydrotreating of residue.
- Chapter 9 presents experimentation in large-scale continuous ebullated-bed reactors. Details of the characteristics of this type of reactor are given, such as different parts of the reactor, advantages and disadvantages, catalyst issues, and sediment formation. Various experimental tests are described in detail in terms of the effect of reaction conditions on impurities removal, conversion, composition of products, and hydrogen consumption.
- Chapter 10 details experimentation in continuous stirred tank reactors. A series of experiments are described, such as hydrocracking of an atmospheric residue, parallel thermal and catalytic hydrotreating of heavy oil, and deactivation of a hydrotreating catalyst.

Each chapter provides detailed information and step-by-step procedures for each level of experimentation for conducting correct hydrotreating experiments. Examples of the evaluation of reaction conditions, type of feed, type of catalyst and support, with different characterization techniques for petroleum feedstocks and for fresh and spent catalysts, as well as experiments for determining mass transfer limitations and deviation from ideality of flow pattern are thoroughly described with the aid of detailed experimental data collected from the different reaction scales.

Experimental data, explanations of how to conduct hydrotreating tests, calculations, interpretation of results, and rigorous treatment of the different topics involved in the development of hydrotreating processes and catalysts make this book an indispensable reference not only for professionals working in the area of catalytic hydrotreating, but also as a textbook for full courses in chemical reaction engineering, in which experimental topics on catalytic hydrotreating and other reactions are discussed.

It is expected that *Experimental Methods for Evaluation of Hydrotreating Catalysts* will quickly become an outstanding and distinctive book because it emphasizes detailed descriptions of the different reaction scales that are used for evaluating hydrotreating processes and catalysts, gives details of experimental setups, methodologies, and characterizations, and provides a series of examples focused on the evaluation of different reaction parameters and catalysts with a variety of petroleum feedstocks.

Jorge Ancheyta

1

Experimental Setups for Hydrotreating of Petroleum Fractions

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1.1 Introduction

The development of catalyst and process technologies for hydrotreating petroleum fractions is a complex task that includes performing experiments at different reaction scales, so-called scaling-up. All experimental scales are equally important since a full understanding of all factors that can affect the performance of different hydrotreating reactions should be considered. For example, hydrodynamics and transport properties are responsible for mass transfer between phases and these ultimately have an impact on the production of any specific product. In lower-scale experiments, it is necessary to understand factors that could be responsible for changes in the development of a reaction, such as deactivation of the catalyst by intermediate products of the reaction, deposition of large molecules on the active sites of the catalysts or molecular changes in the active compounds due to changes in the oxidation states of active catalytic species. When a chemical reaction is being investigated, it usually follows a scale-up process before it becomes an industrial process. It stars at micro-reactor level where the feasibility of the process is tested and if results are promising it is moved one level up to bench scale and/or then to pilot plant scale, semi-commercial scale, and finally it becomes an industrial process. At the early stages of experimentation there is preliminary research to evaluate the feasibility of any chemical process. This proof of concept step involves carrying out a series of carefully planned experimental tests that provide sufficient information on whether to continue or discard this new approach. When results are encountered, encouraging the information compiled through this stage is key to providing the intrinsic kinetic model of the reaction, the type of reactor needed, catalyst, hydrodynamics, optimum operational conditions, and limiting issues of the reaction, among other valuable information.

It is then important to have clear idea about the characteristics of the reactors used in the different evaluation scales. This chapter describes the advantages and disadvantages of the operation modes and type of reactors used during hydrotreating, which can be used as a guide for designing catalysts and new processes.

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1.2 Type of Operation

In terms of the type of operation, there are three main modes of operation of experimental units. The most simple and common is batch, where reactants are loaded into the reactor at the beginning of the operation and products and unreacted chemicals are collected at the end. In hydrotreating reactions, the consumption of hydrogen might cause the total pressure of the system to decrease, therefore the ratio of hydrogen to heavy oil will decrease over time and only is known at the beginning of the experiment.

On the other hand, if isobaric operation is required, hydrogen can be added through the course of the reaction to maintain the pressure of the system while liquid remains stationary. This type of operation is known as semi-batch. Both batch and semi-batch operations require a minimum amount of reactants and some additional equipment compared with continuous operation. Something important to consider is that in non-continuous operation, the initial reaction time is uncertain. It is commonly accepted that the initial reaction time starts once all reactants are confined in the reactor and operating conditions have been reached. Consequently, it is difficult to confirm that prior to reaching this point, reactants were unaffected by heating or pressurization of the system. Batch and semi-batch operations are performed in three steps: loading and preparation of reactants (heating and pressurization), reaction, and product separation and quantification.

Continuous operation represents a more challenging task in terms of design, construction, and operation. Similar to the non-continuous mode, the experimental reaction in continuous systems comprises three well-defined sections: delivery and preparation of feedstocks, reaction, and product separation and quantification. In the first section, reactant flow rates are established and operating conditions are met before the streams enter the reactor. The reaction section comprises only the reactor. In the product separation and quantification section, the products leaving the reactor are conditioned for subsequent quantification and analysis. In continuous operation a certain amount of time should be allowed before the unit reaches steady-state operation.

Batch reactors are preferred at early stages of research because they require the least equipment and are easy to operate. Continuous operation is more demanding in terms of experimental equipment and operational costs. Table 1.1 summarizes the operational characteristics of the three types of processes. Although some aspects of the hydrotreating catalyst and process influence the decision regarding the type of operation, the selection of any particular type of operation depends entirely on the scope of the experimentation and the economical resources available.

1.3 Selection of the Reactor

The success of scaling-up any chemical process is based on the reliability of experimental data collected. As the chemical reactor is the centre of any chemical process, the reactor selected will impact on the accuracy of the experimental information produced from it. The reactor selection is determined by the nature of the chemical reaction being studied and the aim of the experimental results obtained from it. It is important to identify, for example, the number of phases involved, the compositions of the streams, the complexity of the

Table 1.1 Comparison of operation in batch, semi-batch, and continuous experimental setups.

	Type of operation		
Factor considered	**Batch**	**Semi-batch**	**Continuous**
Amount and cost of equipment	Low	Intermediate	High
Cost of installation	Low	Low	High
Cost of operation	Low	Intermediate	High
Ease of operation	Easy	Easy	Complicated
Amount of reactants required	Low	Intermediate	High
Operational safety	Safer	Safer	Safe
Resemblance with industrial operation	Low	Intermediate	High

Table 1.2 Summary of information required for designing catalytic reactors.

Catalyst design	**Reactor design**	**Catalytic reactor design**
Mechanical and flow properties	Kinetics of the reaction	Reaction conditions
Catalytic properties	Mass balance	Catalyst type
Physical and chemical properties	Momentum and energy balance	Type of reactor

reaction paths, the range of operating conditions, the heat generated or consumed by the reaction, the possible reaction products, the characteristics of the catalyst (size and shape) or sampling of products, among others. The selection of the reactor depends on the available information on mass and energy balances as well as the chemical kinetics of any specific reaction. The aim of performing experiments is invariably to provide reliable technical information to discard or continue with the next step of process development.

Table 1.2 summarizes the three main parameters required for designing a catalytic reactor as suggested by Bartholomew and Hecker (1994). Since the kinetics of the reaction might be not known, the reactor volume cannot be calculated directly, but previous experimental information on similar reactions can provide a sensible estimate of the size of the reactor needed for any particular application.

1.4 Experimental Considerations for the Operation of the Laboratory Reactor

It should be pointed out that if the main purpose of the reactor is to develop kinetic studies of reactions only chemical reactors with a flow pattern close to ideal models should be considered. Any real chemical reactor has its operational boundaries in the performance of the continuous stirred tank (maximum mixedness) and the plug-flow reactor (completely segregated) (Nauman 2008). For this reason, it is important to consider that if chemical kinetics studies will be performed, the stirred tank reactor operating in batch, semi-batch, and continuous mode should be considered first. The main disadvantage of the bubble column and fluidized bed reactor in chemical kinetics is their poor performance due to the poor backmixing. These reactors should operate with a high ratio of recirculation to resemble the conditions of maximum mixedness characteristic of stirred tank reactors. If operation close to an ideal reactor can be achieved, the kinetics of the reaction can be obtained from a relatively simple mathematical expression. For catalyst exploration and evaluation there is no restriction on the type of reactor but the results should be cautiously interpreted.

At laboratory level it is not surprising to find mainly continuous stirred tank reactors, although at industrial level these reactors are rarely used except for very specific operations (Donati and Paludetto 1999), and very often experimental data obtained from stirred tanks are used for scaling-up or optimizing the operation of industrial reactors. It is difficult to pick out an ideal experimental reactor because its selection will depend on many factors. Basically, stirred tank reactors offer the highest flexibility of all reactors because they can be operated in batch or semi-batch without any major changes in the experimental setup or in a continuous mode. This type of reactor is perfect for kinetic studies provided that deviations from ideal behaviour are minimal (gradientless in temperature and concentration).

If premixing of the streams before entering the reactor is envisioned in the experimental plant design, static mixers should be considered for the operation (Stankiewicz and Moulijn 2000). Mixing devices can be chosen for the operation depending on the flow regime (laminar, transition, or turbulent) of the streams but static mixers are suitable for gas–liquid mixing independently of the flow regime. Static mixers improve considerably the axial mixing of both phases and because of this they can even be used as a double-purpose devices (mixing and reaction). If mixing of the streams is not accomplished in a static mixer, it is usually good practice to allow a minimum distance of one hundred times the internal diameter of the tubing before entering the following stage in the process (Trambouze et al. 1984).

Sampling is critical in kinetic studies and perhaps a difficult operation to accomplish in any type of process. If it is carried out in a non-steady-state reactor the volume of the sample should not affect the total volume of the reactor. Sampling should be carried out in a system that allows fast cooling and efficient storage to avoid any misinterpretation of the data.

Another possible operational problem encountered in hydrotreating, particularly when heavy oils are processed, is the possibility of plugging in the equipment (Pang et al. 2009). Cracking of long hydrocarbon chains inevitably produces coke and sludge, which can reduce operational efficiency.

Mixing is the main factor that overcomes the mass transfer resistance in the reactor but it only affects the gas–liquid resistance and consequently other factors might be varied (Levenspiel 1999). In order to lower the liquid–solid resistance, small catalyst particles with high superficial area can be used. To avoid pore diffusion the use of very small particles is recommended. In an experimental plan, it is useful to vary some of the reaction parameters (agitation speed, catalyst loading, catalyst size, hydrogen concentration, reactants flow rate, total pressure of the system) between experiments to identify any major contribution of the operational parameters.

1.5 Considerations for Experimental Reactor Configuration

There are no standard guidelines for designing an experimental setup on an industrial scale. At laboratory reactor level, the design relies more on previous experience with a similar process or adapting an already installed experimental setup to cope with new catalyst and process needs. The experimental setup is divided into three main stages (non-steady operation) or sections (steady operation): delivery and preparation, reaction and separation, and cooling, depressurization and sampling. Once the reactor and mode of operation have been defined, the next stage is to calculate the mass and energy balance of the complete operation. After the laboratory setup has been configured, it is advisable to carry out a simulation of the experimental plant using a process software simulator to identify any additional process equipment required (such as phase separators, heat exchangers, etc.) and any probable cause of error in the mass balance (i.e. loss of light hydrocarbons in certain parts of the unit) in certain sections of the plant. The rest of the equipment will be selected according to the mode of operation of the experimental setup.

1.5.1 Configuration for Batch and Semi-batch Operation Modes

These two modes of operation result in the lowest investment in laboratory equipment. Stirred tank reactors are usually chosen as laboratory reactors for this type of operation. Figure 1.1 shows a simple process diagram of the experimental setup. In the diagram the hydrogen is supplied by gas cylinders connected directly to the reactor. The total mass balance is carried out by measuring accurately the initial amount or flow of hydrogen and hydrocarbon, and liquid and gas product streams. Liquid product quantification might be determined by weighing before storage for subsequent analysis while gas quantification requires a flow meter for total gas quantification and online analysis by gas chromatograph. The gas product stream contains mainly unreacted hydrogen and a mixture of reaction products that comprise mainly light hydrocarbons and hydrogen sulfide. A scrubber is located before venting the gases to remove mainly hydrogen sulfide from the stream.

In the case of semi-batch operation hydrogen is added continuously from the cylinders. In batch mode the decay of pressure by the reaction consumption is never compensated

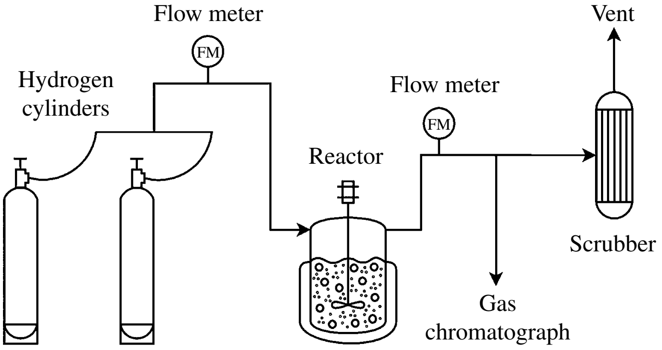

Figure 1.1 Experimental setup for hydrotreating in batch and semi-batch operation modes.

and the ratio of hydrogen to hydrocarbon remains uncertain after the beginning of the experiment.

If a sampling system is required, it should cool down the samples immediately once they leave the reactor. Another cooling system is needed to stop the reaction from proceeding in the vessel when the experiment is complete.

The experimental setup shown in Figure 1.1 is not the only possible configuration. Changes can be made depending on the additional services available at the installation site or any special requirements of the process. It is advisable for environmental and safety reasons to burn the gas effluent instead of venting it to the atmosphere.

1.5.2 Configuration for Continuous Operation

The continuous mode requires more control of the inlet and outlet streams. Figure 1.2 shows a simplified diagram of the configuration of an experimental setup for continuous operation. This unit is shown with a continuous stirred tank reactor, but a tubular reactor could also be used. Flow meters are located at inlet and outlet streams and provide a mass flow rate reading in order to reduce the error due to changes in the temperature and pressure of the stream. One tank is needed to feed the hydrocarbon into the reactor and another for product collection. Before entering the reactor both streams should be conditioned to reaction pressure and temperature. The streams can be mixed in the reactor or before the reactor but in the latter case a mixing device should be installed. Static mixers are preferred but simpler devices like tees might be used instead if there is enough distance between the mixing point and the subsequent operation.

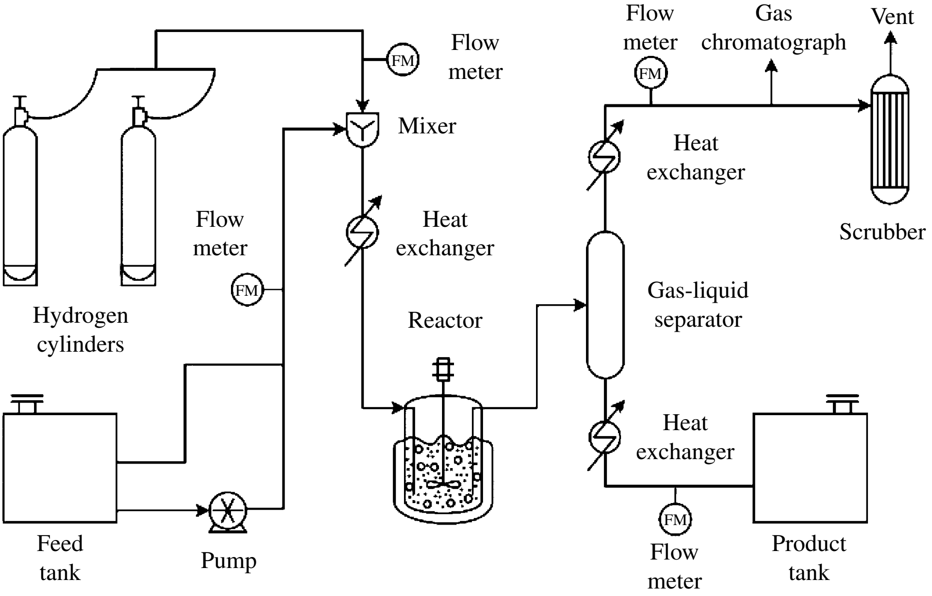

Figure 1.2 Experimental setup for hydrotreating in continuous operation mode.

Once the reacting mixture leaves the reactor, it enters a gas–liquid separator. After leaving the separator, the gas and liquid should be conditioned for storage and analysis. It is worth pointing out that liquid product can block process lines when heavy oils are processed if the operation temperature is close to ambient. On the other hand, gas should be analysed online to minimize any error in the mass balance of the system. A simulation of the system should be able to identify the product distribution and expected flow rate of the streams. The latter is useful to identify the amount of light hydrocarbons that is dissolved in the liquid effluent and the amount and distribution of hydrocarbons that leave the separator with the gas stream and which might not be analysed by the gas chromatograph.

1.6 Analysis of Products

Different analytical procedures are carried out in order to determine the composition, properties, and/or characteristics of the hydrotreating reaction products.

1.6.1 Gases

The quantification of gas phase products (H_2, H_2S, and C_l–C_5 hydrocarbons) is carried out in a gas chromatograph. Chemical species are separated in molecular sieve columns and identified by a thermal conductivity detector (TCD) and flame ionization detector (FID) (Del Bianco et al. 1994; Kennepoh and Sanford 1996; Siewe and Ng 1998; Dehkissia et al. 2004).

1.6.2 Liquids

The liquid oil fraction is recovered from the reactor for subsequent analysis. The purpose is to obtain valuable information about the boiling range distribution, elemental composition (C, H, O, N, and S), impurities content, and to determine properties such as viscosity, American Petroleum Institute (API) gravity, etc. The following are some examples of the characterization techniques used to analyse liquid hydrocarbons.

- *Boiling range distribution*. The oil fraction product is commonly analysed by gas chromatography (GC) temperature simulated distillation (SIM-DIST) and/or high-temperature simulated distillation (HTSD). SIM-DIST is a useful analytical method because it is quick and easy to use. This technique allows the elution of hydrocarbons containing up to 120 carbon atoms, using capillary columns with standing temperature up to 440 °C (Bacauda et al. 1998). It can identify four pseudocomponents distinguished by their boiling points: naphtha (initial boiling point [IBP]–216 °C), distillates (216–343 °C), vacuum gas oil (343–545 °C), and residue (545 °C+), according to the ASTM D2887 method. Thermogravimetric analysis (TGA) is sometimes also used, which is discussed in later chapters. HTSD using GC is based on the determination of the true boiling point (TBP) distribution of petroleum products up to a final boiling point (FBP) of 720 °C and it is recommended for analysis of samples containing distillation residua. It uses thermally stable wide-bore capillary columns which have certain advantages over packed columns, for example better column stability and life, lower column bleed, faster analysis, elution of higher boiling petroleum fractions, compatibility with automated on-column injection, and improved reproducibility. Nowadays, the ASTM D7169-11 method extends the boiling point profile up to 720 °C (corresponding to the elution of n-C_{100}), targeting high molecular weight hydrocarbons that do not easily elute out of a GC column.

- *Elemental analysis*. The analysis of petroleum to determine the percentages of carbon, hydrogen, nitrogen, oxygen, and sulfur (C, H, N, O, and S) is perhaps the first method used to examine the general nature and perform an evaluation of a feedstock and hydrocracked products. The analyses are carried out in an elemental analyser (e.g., CHN-2000 from LECO) according to ASTM D-5185 methods. The atomic ratios of the various elements to carbon (i.e. H/C, N/C, O/C, and S/C) are frequently used as indicators of the overall character of the feedstock and products. It is also of value to determine the amounts of trace elements, such as vanadium and nickel, in a feedstock since these materials can have serious deleterious effects on catalyst performance during refining by catalytic processes (Speight 2007). The ASTM methods for ultimate elemental analysis of petroleum products are illustrated in Figure 1.3.
- *Metal content*. A variety of tests (ASTM D-1026, ASTM D-1262, ASTM D-1318, ASTM D-1368, ASTM D-1548, ASTM D-1549, ASTM D-2547, ASTM D-2599, ASTM D-2788, ASTM D-3340, ASTM D-3341, and ASTM D-3605) have been designated for the determination of metals in petroleum products. Determination of metals in whole feeds can be accomplished by combustion of the sample so that only inorganic ash remains. The ash can then be digested with acid and the solution is examined for metal species by atomic absorption (AA) spectroscopy or inductively coupled argon plasma (ICAP) spectrometry (Speight 2007). The methodology for metal determination includes sample preparation, sample digestion, and metal quantification. Microwave ovens are commonly used for digesting, dissolving, hydrolysing, extracting, or drying a wide range of materials for AA and/or ICAP analysis.
- *SARA composition*. The four SARA fractions are saturates (S), aromatics (A), resins (R), and asphaltenes (A). The SARA fractionation method usually starts with the removal of asphaltenes by precipitation with a saturated hydrocarbon (n-pentane or n-heptane) (Shuyi et al. 2008; Galarraga and Pereira-Almao 2010) as described by the ASTM D3279 method (Trejo et al. 2004). The following separation of the three remaining fractions (SAR) is then accomplished by elution with a series of increasingly polar solvents as mobile phases in accordance with the ASTM 2700 method to obtain the concentrations of saturates, aromatics, and resins (Luo and Gu 2007; Molina et al. 2010). Saturates are

Hydrogen	ASTM: D–1018, D–3178, D–3343, E–777
Nitrogen	ASTM: D–3179, D–3228, D–3431, E–148, E–258, E–778
Oxygen	ASTM: E–385
Sulfur	ASTM: D–124, D–1266, D–1552, D–1757, D–4294

Figure 1.3 ASTM methods used for determining H, N, O, and S.