NTNU – Trondheim
Norwegian University of
Science and Technology

Production and processing of sour crude and natural gas - challenges due to increasing stringent regulations

Darkhan Duissenov

Petroleum Engineering
Submission date: June 2013
Supervisor: Jon Steinar Gudmundsson, IPT

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Abstract

The worldwide demand for petroleum is growing tremendously. It is expected that the demand will have incremental capacity of 20 mb/d for crude oil, reaching 107.3 mb/d, and demand for natural gas will rise nearly 50% to 190 tcf in 2035, compared to 130 tcf now. According to the International Energy Agency 70% of crude oil reserves and 40% of natural gas reserves are defined as having high content of organosulfur compounds. Obviously, for decades to come, to satisfy the growing global needs for fossil fuels, reservoirs with sour contaminants will be developed intensively.

The sulfur compounds in crude oils and natural gas generally exist in the form of free sulfur, hydrogen sulfide, thiols, sulfides, disulfides, and thiophenes. These compounds can cause considerable technical, environmental, economic, and safety challenges in all segments of petroleum industry, from upstream, through midstream to downstream.

Currently, the sulfur level in on-road and off-road gasoline and diesel is limited to 10 and 15 ppm respectively by weight in developed countries of EU and USA, but this trend is now increasingly being adopted in the developing world too. Furthermore, it has to be expected that the sulfur level requirements will become more and more strict in the foreseeable future, approaching zero sulfur emissions from burned fuels.

The production of ultra low sulfur automotive fuels has gained enormous interest in the scientific community worldwide. Oxidative desulphurization, biocatalytic desulphurization, and combined technologies, which are alternatives to conventional hydrodesulphurization technology, are much more efficient and more economical in removing complex sulfur compounds, especially benzothiophene, dibenzothiophene and their alkyl derivatives.

Keywords: *product quality specifications,* H_2S *corrosion, hydrodesulphurization, biocatalytic desulphurization, oxidative desulphurization*

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1. Introduction

Fossil fuel-based hydrocarbons are a primary energy source for current civilizations, which nowadays accounts for 83% of global energy consumption, and this tendency is forecasted to continue even after two decades (Pratap, 2013). However, to satisfy such rapidly growing appetite for fossil fuels, the petroleum industry will have to face a lot of challenges. Oil and gas companies, which have always preferably produced the oil and gas from the reservoirs technically the easiest to develop, will have to develop more complex and extremely challenging sour hydrocarbon projects. In the nearest future, crude oil and natural gas with high sulfur content will be the energy source of choice to meet increasing demand.

In order to understand the importance of those challenges thorough analysis of hydrocarbon quality is needed. To start with, it should be that the value of the reservoir fluid is commonly based on its quality characteristics. Lower quality Dubai crude is sold at discount rate to lighter, sweeter Brent crude. Sulfur content is among the most important characteristics of the crude oil and natural gas. Currently, there is a negative trend of increase of sulfur content in hydrocarbons worldwide. If US sulfur content of crude oil input to refineries was 0.88% in 1985, as of February 2013 it was 1.44% (EIA, 2013).

Another unfavorable for refineries tendency regards to environmental sulfur regulations. If in 2012 the maximum allowable level of sulfur was 795 ppm in Africa, 605 ppm in the Middle East, 520 ppm in Latin America, in 2030 it is expected to decrease the sulfur content to 95 ppm, 16 ppm, and 30 ppm respectively. The other nations of the world are moving towards environmentally friendly transportation fuels too. New transportation fuel specifications are being put into effect worldwide. As a result, those contradirectional factors, such as hydrocarbon quality deterioration and reducing the maximum allowable level of sulfur, are making the situation even worse.

However, before considerable investment will be put in completely new technologies and tools, the industry has to deal with existing problems. There are number of technical, economical, and environmental problems. All of them are caused by the presence of organosulfur compounds in petroleum. They are very undesirable, because of their actual or potential corrosive nature, disagreeable odor, deleterious effect on color or color stability, and unfavorable influence on antiknock and oxidation characteristics. Furthermore, sulfur compounds poison expensive refining catalysts and pollutes into the atmosphere in a form of sulfur oxides when burned, causing environmental problems. Emissions of sulfur compounds formed during the combustion of petroleum products are the subject of environmental monitoring in all developed countries.

Crude corrosivity problems have been studied since 1950's mostly because of their severity and economic impact on production and refining operations. To date the annual cost of corrosion worldwide is estimated at over 3% of GDP of the planet, which is literally 3.3$ trillion. Without taking into account the progress made in understanding the role of different parameters on the corrosion process, modern scientific society cannot give exact answers in understanding and prediction of petroleum corrosivity.

Hydrocarbon producing companies in order to meet the stringent environmental and safety requirements are in search of "green" and cost-effective methods for desulphurization of crude oil and natural gas. Desulphurization is costly technology and petroleum refiners could spend 25 billion USD over the next decade (Monticello, 1996). Commonly used conventional desulphurization technology - hydrodesulphurization - is expensive and does not efficiently handle sulfur removal in a number of situations. Hence, other efficient desulphurization technologies, as biocatalytic desulphurization, oxidative desulphurization are being used in test scale and commercial scale projects.

The main purpose of this master thesis is to analyze the rising sulfur problem and outline the needs for better technologies to remove the sulfur. The analysis has been done based on annual energy reviews, from different sources, such as OPEC, BP, EIA, and others. The origin and the types of sulfur present in hydrocarbons are studied. Also commercial, semi-commercial, and test scale desulfurization technologies are reviewed.

2. World petroleum reserves

British Petroleum defines the term proved reserves of crude petroleum as those quantities of petroleum that geological and engineering information indicates with reasonable certainty can be recovered in the future from known reservoirs under existing economic and operating conditions (BP, 2012).

As of January 2013, the estimated world proved reserves of crude petroleum were 1.6 billion barrels. OPEC currently accounts for 73.6% of total world oil reserves. Venezuela with its heavy, sour crude holds the largest share of the world's petroleum reserves at 18% of the total, as a result of recent reserves identified in this country. Other countries with the biggest crude oil reserves are Saudi Arabia (16.2%), Canada (10.6%), Iran (9.4%) and Iraq (9.6%) (Table 20).

On a regional basis, the Middle East accounts for nearly 48% of the world's reserves. Central and South America is second with 20%, following recent reserves identified in Brazil and Venezuela, and North America is third with 13% (Figure 1).

The International Energy Agency (IEA) estimates that 70% of the world’s remaining oil reserves consist of heavy, high sulfur crude. Moreover, there is a common tendency in all big discoveries found in the last 30 years. The crude from these new oil fields tends to be heavy, difficult to extract, with high sulfur content. One of the reasons of crude oil quality deterioration is depletion of production from conventional, commonly sweet reservoirs. This trend can be seen by looking at the history of crude oil production, which is now extending over more than 150 years (Zittel & Schindler, 2007):

- Virtually all the world's largest oil fields were all discovered more than 50 years ago;
- Since the 1960s, annual oil discoveries tend to decrease;
- Since 1980, annual consumption has exceeded annual new discoveries;
- Till this day more than 47,500 oil fields have been found, but the 400 largest oilfields (1%) contain more than 75% of all oil ever discovered;

When it comes to natural gas proved reserves the Middle East and Europe & Eurasia region account for 75% of whole world’s reserves (Figure 2). In fact, 40% of the world’s natural or associated gas reserves currently identified as remaining to be produced, representing over 2600 trillion cubic feet (tcf), are sour, with both H_2S and CO_2 present most of the time. Among these sour reserves, more than 350 tcf contain H_2S in excess of 10%, and almost 700 tcf contain over 10% CO_2 (Lallemand et al., 2012).

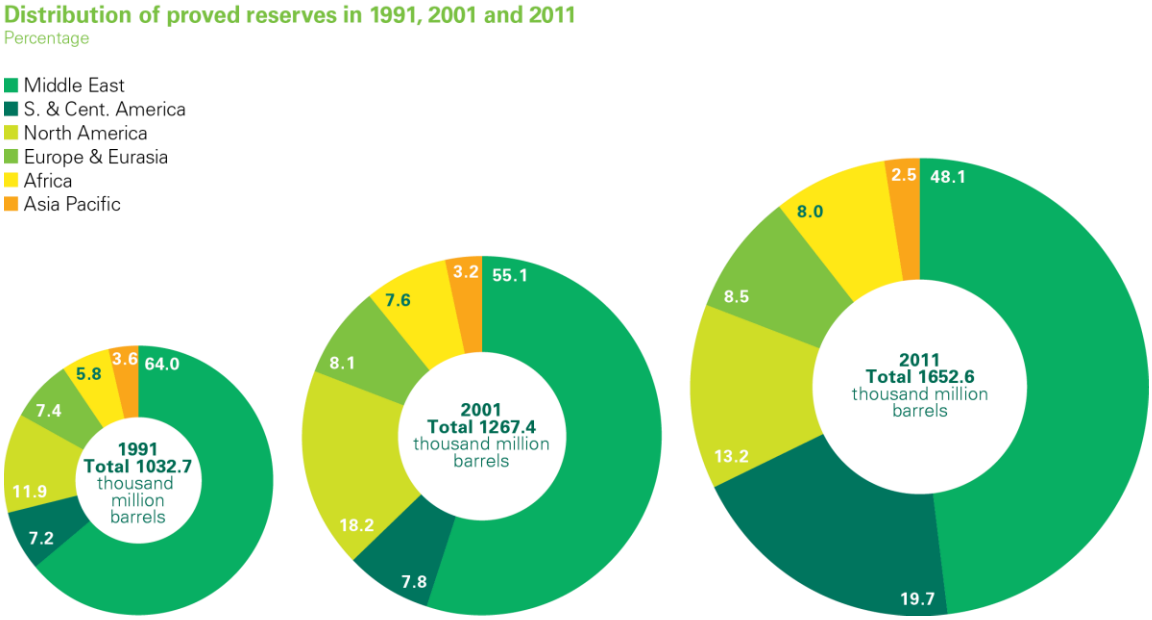


Figure 1 *Distribution of proved reserves of crude oil in 1991, 2001 and 2011 (BP, 2012)*

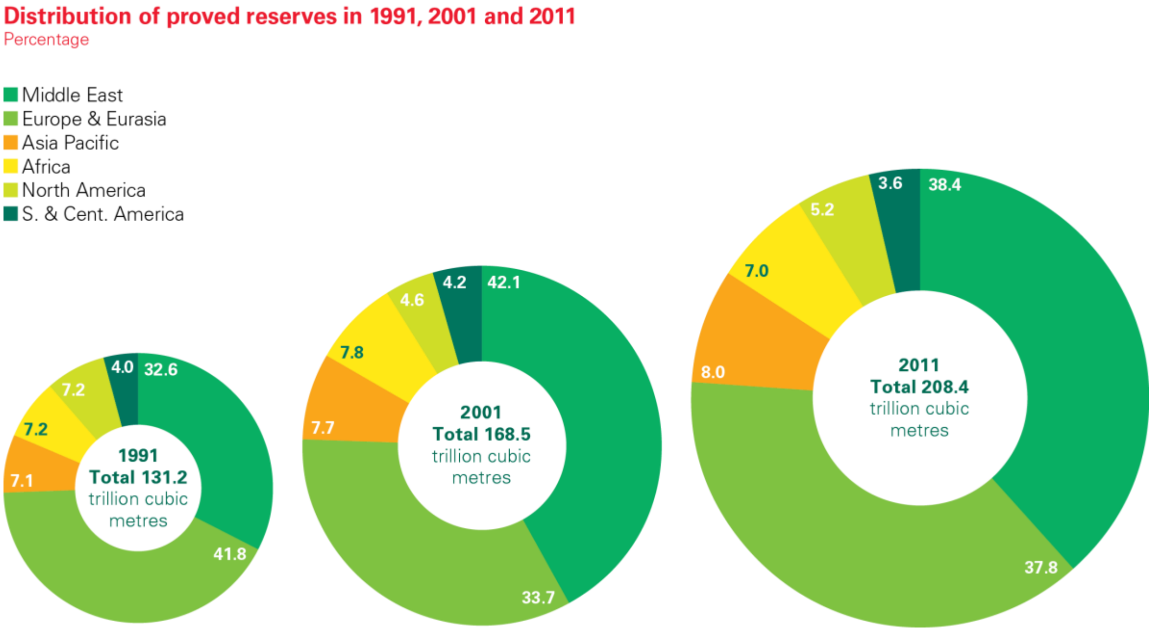


Figure 2 *Distribution of proved reserves of natural gas in 1991, 2001 and 2011 (BP, 2012)*

3. Petroleum supply and demand outlook

Worldwide crude oil production is forecasted to increase to meet the growing consumption, at the same time the sources of growth will change the global balance. Global crude oil supply is set to rise by about 16.5 Mb/d by 2030. 75% of the global supply growth will be accounted to OPEC. Crude supply decline from Europe, Asia Pacific, and North America is expected to offset by growth in deepwater Brazil and the FSU (BP, 2011).

Non-OPEC output will rise by nearly 4 Mb/d. Unconventional supply growth should more than offset declining conventional output, with biofuels adding nearly 5 Mb/d and oil sands rising by nearly 2 Mb/d (BP, 2011).

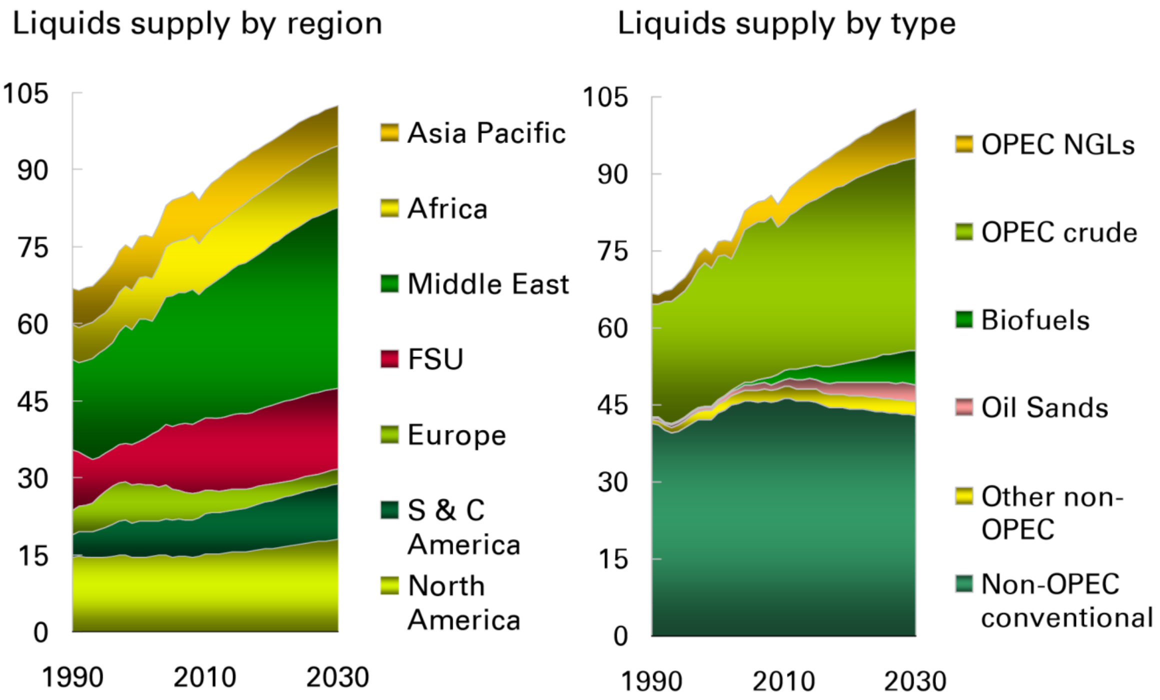


Figure 3 *Worldwide petroleum liquids supply outlook (BP, 2011)*

The global crude oils demand is also predicted to increase, but growth slows to 0.8% p.a. (from 1.4% p.a. in 1990-2010 and 1.9% p.a. in 1970-90). The OPEC is forecasted the demand for crude oil for long-term period from 2010 to 2035. The outlook for oil demand is shown in Table 1. In the forecasting period of 25 years demand will have an incremental capacity of 20 mb/d, reaching 107.3 mb/d by 2035. 87% of the increase in crude oil demand in developing Asia, whereas OECD demand shows a steady decline, as it was already peaked in 2005 (OPEC, 2012). Non-OECD consumption is likely to overtake the OECD by 2014, and reach 66 Mb/d by 2030.

Table 1 *World oil demand outlook (mb/d) (OPEC, 2012)*

	2010	2015	2020	2025	2030	2035
OECD America	24.1	23.7	23.5	23.0	22.4	21.7
OECD Europe	14.7	13.7	13.4	13.0	12.6	12.1
OECD Asia Oceania	8.1	8.4	8.2	8.0	7.6	7.3
OECD	**46.8**	**45.8**	**45.2**	**44.0**	**42.6**	**41.1**
Latin America	4.9	5.4	5.8	6.1	6.4	6.6
Middle East & Africa	3.3	3.8	4.1	4.5	4.8	5.1
India	3.3	4.0	4.9	6.0	7.4	9.0
China	9.0	11.1	13.2	15.0	16.4	17.6
Other Asia	6.8	7.5	8.4	9.1	9.7	10.3
OPEC	8.1	9.0	9.8	10.6	11.4	12.0
Developing countries	**35.4**	**40.8**	**46.3**	**51.3**	**56.0**	**60.6**
Russia	3.2	3.5	3.6	3.6	3.6	3.6
Other Eurasia	1.6	1.7	1.8	1.9	2.0	2.1
Eurasia	**4.8**	**5.2**	**5.4**	**5.5**	**5.6**	**5.6**
World	**87.0**	**91.8**	**96.9**	**100.9**	**104.2**	**107.3**

The transportation sector is a key to future oil demand growth. OECD consumption will fall to 40.5 Mb/d. Figure 4 shows the increasing tendency in oil consumption in road transportation. It can be easily seen that by 2020, non-OECD oil use in road transportation (nearly 14 Mb/d) will be greater than in the OECD. Furthermore, the majority of this increase will be dominated by developing Asian countries, especially China and India.

Demand for natural gas will rise nearly 50% to 190 tcf in 2035, compared to 130 tcf for now. Gas demand in the forecasting period will be mainly driven by non-OECD countries, with growth averaging 3% p.a. to 2030 (Figure 5). On the top of the demand growth is non-OECD Asia (4.6% p.a.) and the Middle East (3.9% p.a.). Of the major sectors globally, growth is fastest in power (2.6% p.a.) and industry (2% p.a.) which matches with historic patterns., Compressed natural gas use in transport is confined to 2% of global transport fuel demand in 2030, with threefold increase from today’s level (BP, 2011).

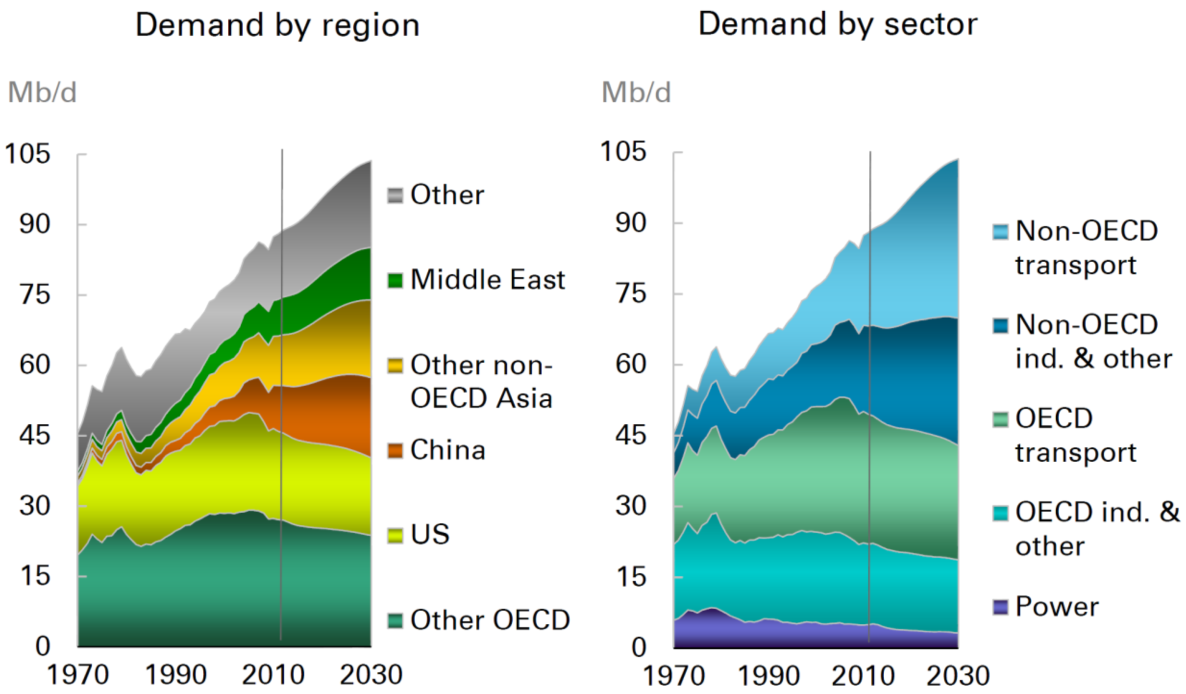


Figure 4 *Worldwide petroleum liquids demand outlook 1970-2030 (BP, 2013)*

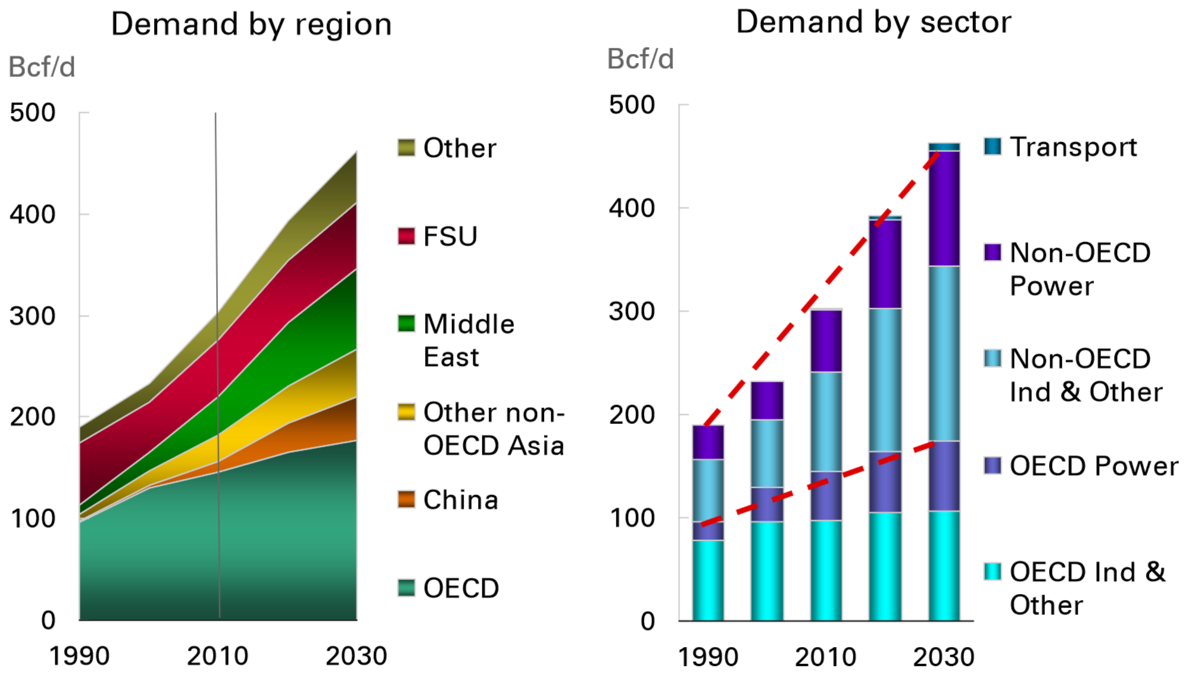


Figure 5 *Worldwide gas demand outlook 1990-2030 (BP, 2011)*

4. Crude quality outlook

4.1 Density and API gravity of crude oil

Crude oil quality is measured in terms of density and divided into four groups such as light, medium, heavy and extra heavy crudes (Figure 6). Those groups are defined depending on the value of degrees API. Density in degrees API is a unit of measurement of oil density, developed by the American Petroleum Institute. Measurement of degrees API allows us to determine the relative density of oil to the density of water at the same temperature of 15.6 degrees Celsius. The API degree is found with the following formula:

$$API = \frac{141.5}{SG} - 131.5$$

The SG stands for specific gravity or relative density, which is equal to the density of the substance divided by the density of water (density of water is 1000 kg/m^3). So if the API gravity is greater than 10, then the oil is lighter and floats on water, and if less than 10, then drowned (Wikipedia, 2012). API gravity was designed so that most values would fall between 10° and 70° API gravity (Schlumberger, 2012).

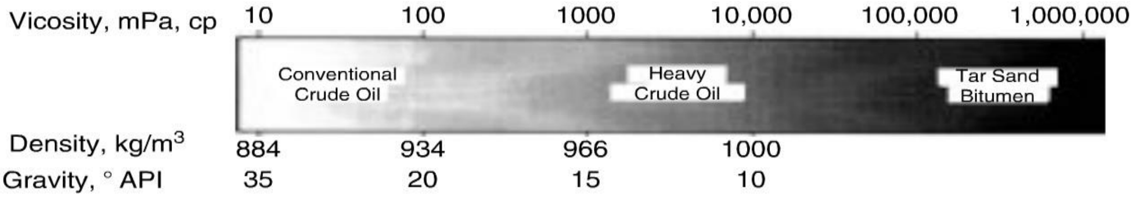


Figure 6 *Classification of petroleum, heavy oil, and bitumen by API gravity and viscosity (Speight, 2007)*

Depending on API gravity crude oils are classified as follows (Figure 6):

- Light: API>31.1
- Medium: 22.3<API<31.1
- Heavy: API<22.3
- Extra heavy: API<10.0

4.2 Sweet and sour crude oil

Depending on the amount of sulfur the crude oil can be sweet or sour. When the total sulfur level in the oil is less than 0.5 % the oil is called sweet and if it is more than that the oil is called sour. Sweet crude oil is more preferred by refineries as it contains valuable chemicals which is needed to produce the light distillates and high quality feed stocks.

Historically, early prospectors tasted the crude oil to determine its quality. Crude petroleum had a sweet taste and pleasant smell if the content of sulfur was low. For this reason, sweet crude is a low sulfur crude oil (FSU, 2010).

Sweet crude is easier to refine and safer to extract and transport than sour crude. Because sulfur is corrosive, light crude also causes less damage to refineries and thus results in lower maintenance costs over time.

Major locations where sweet crude is found include the Appalachian Basin in Eastern North America, Western Texas, the Bakken Formation of North Dakota and Saskatchewan, the North Sea of Europe, North Africa, Australia, and the Far East including Indonesia.

Table 2 *Quality levels - API gravity and sulfur content (Eni, 2012)*

Crude Oil Class	Property Range	
	Gravity (ºAPI)	Sulfur (wt. %)
Ultra Light	>50	<0.1
Light & Sweet	35-50	<0.5
Light & Medium Sour	35-50	0.5-1
Light & Sour	35-50	>1
Medium & Sweet	26-35	<0.5
Medium & Medium Sour	26-35	0.5-1
Medium & Sour	26-35	>1
Heavy & Sweet	10-26	<0.5
Heavy & Medium Sour	10-26	0.5-1
Heavy & Sour	10-26	>1

As opposed to sweet crude sour crude is sold at a discount to lighter sweeter grades. Because the sulfur compounds in the crude oils are generally harmful impurities, they are toxic, have an unpleasant odor, contribute to the deposition of resin and in combination with water causes intense corrosion (K-Oil, 2012). Even though it does not restrains the production of inconvenient crude and the data shows that from 1995 to 2011 medium-sour and sour crude has been the major hydrocarbon produced in the world taking about 55 to 60% of whole crude production, which is shown in Table 22.

Major regions with vast sour crude reserves: North America (Alberta (Canada), United States' portion of the Gulf of Mexico, and Mexico), South America (Venezuela, Colombia, and Ecuador), Middle East (Saudi Arabia, Iraq, Kuwait, Iran, Syria, and Egypt).

4.3 Benchmarks of crude oil

The knowledge of commercial value of the reservoir fluid is of vital importance, as petroleum companies is aimed on getting as much profit as possible. The profit is a function of the cost of petroleum. The cost is based on quality characteristics, such as density and sulfur content which are the most important characteristics of the crude. Depending on the chemical composition and the presence of various chemical elements the term benchmark or market crude should be introduced.

The general concept of benchmarking is to classify crude oil based on its quality. The introduction of grading has become necessary due to the different composition of oil as sulfur content, alkane content and the presence of impurities, in addition to where it is located. For the convenience of trade market and to keep the balance between supply and demand typical benchmarks were created. Prices for other crudes are determined by the differentials to benchmarks (K-Oil, 2012). The major crude oil benchmarks are grouped as follows:

(i) West Texas Intermediate (WTI)

West Texas Intermediate is reference crude, which is produced in Texas. The density is about 40° API and sulfur content ranges from 0.4 to 0.5 %. It is mostly used to produce gasoline and therefore that type of oil is in high demand, especially in the United States and China (UP Trading, 2012).

(ii) Brent Blend

Brent is a reference grade of oil from the North Sea. The oil price of Brent is in the basis for the pricing of about 40% of world oil prices from 1971. The word Brent stands for Broom, Rannoch, Etieve, Ness and Tarbat.

(iii) Dubai

Dubai Crude has a gravity of 31° API and a sulfur content of 2 %. It is extracted from Dubai. Dubai Crude is used as a price benchmark because it is one of only a few Persian Gulf crude oils available immediately.

(iv) Tapis Crude

Tapis is the benchmark for light sweet Malaysian crude. The sulfur content is as low as 0.03% and the API gravity is around 45.5. Although this oil marker is not as widely traded as WTI, it is used as a benchmark in Asia (EconomyWatch, 2010).

(v) Bonny Light

Bonny Light is a benchmark for high grade Nigerian crude, with an API of around 36. Due to its very low sulfur content, it corrodes the refinery infrastructure minimally (EconomyWatch, 2010).

(vi) OPEC Basket

OPEC Basket is the pricing data formed by collecting seven crude oils from the OPEC nations (except Mexico). These include Saudi Arabia's Arab Light, Algeria's Saharan Blend, Indonesia's Minas, Nigeria's Bonny Light, Venezuela's Tia Juana Light, Dubai's Fateh and Mexico's Isthmus. This information is used by OPEC to monitor the global conditions of the oil market (EconomyWatch, 2010).

The crude oils represented in Figure 48 are selection of some of the crude oils marketed in various parts of the world. There are some crude oils both below and above the API gravity range shown in the chart (EIA, 2012). Moreover, quality levels as API gravity and sulfur content are presented on Table 23. The classification ranges from ultra-light to heavy and sour and gives the data on daily production.

4.4 Future trends on crude quality characteristics

Crude oil quality, typically measured in terms of API gravity and sulfur content, does, and will increasingly play a major role in determining future refining requirements. Historically, the average quality of crude oil has been declining steadily. Average sulfur content has been increasing considerably and more rapidly than API gravity. And this trend likely to continue for the foreseeable future (MathProInc., 2011).

The detailed analysis on the expected quality changes in oil supply streams with the projection to 2035 are presented in Figures 7 and 8. The figure is projected to improve marginally to around 33.5° API by 2015, from 33.4° API in 2010, and then move back to 33° API by 2035, a level not very dissimilar to the present one. Figure 8 also underscores that the global average for the entire forecast period is anticipated to remain in a fairly narrow range of less than 1° API. Average sulfur content projections are also can be observed (Figure 7). The expected variations in average sulfur content are wider; they are in the range of 10-15% over the 25-year forecast period (OPEC, 2011).

4.5 Product quality specifications

Refined products specification along with quality of crude oil which is used as a feedstock to the refineries another important aspect which significantly influences future downstream investments. In the last 30 years, downstream industry globally has put considerable amount of money in order to meet new petroleum product quality specifications. The very first regulations have affected the lead content in gasoline, and in the middle of 1990s the focus turned to sulfur content in automotive fuel, especially in the most industrialized countries.

The main purpose of those regulations is to yield high quality automotive fuels with sulfur content less than 10 parts per million (ppm). Moreover, regulators want to tighten sulfur content of other refined products, such as fuel oil, marine bunkers and jet fuel.

Some worldwide efforts have already been made to minimize the content of organosulfur compounds in finished products. This can be seen in Figure 49 and Figure 59, which show the global maximum permitted sulfur content in gasoline and on-road diesel fuel, respectively (as of September 2012).

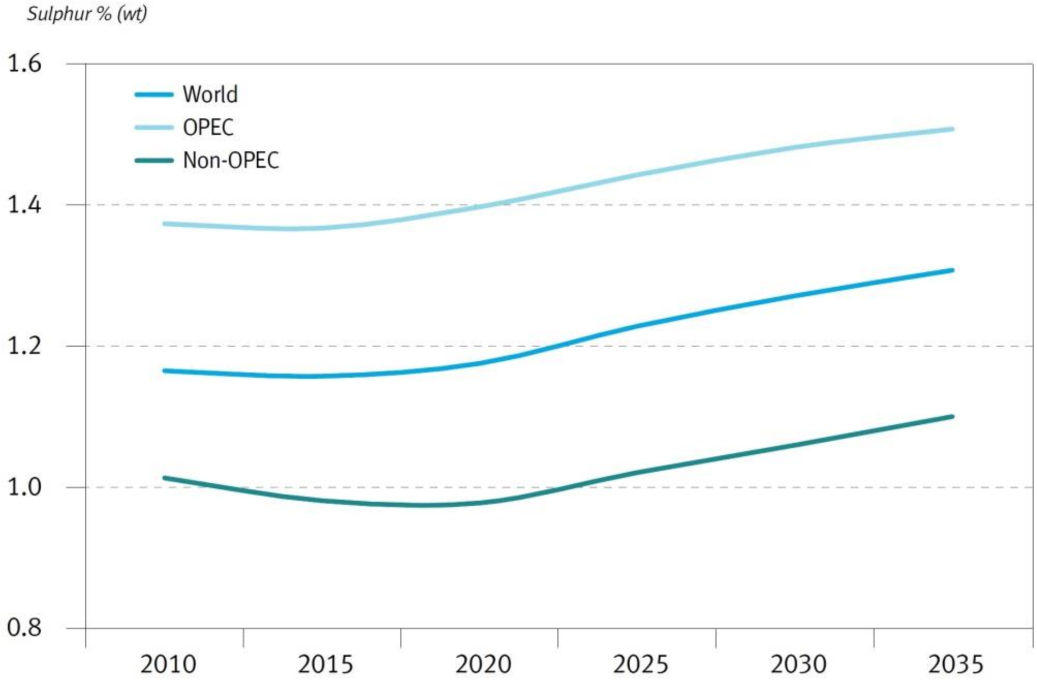


Figure 7 *Crude quality outlook in terms of sulfur content (OPEC, 2011)*

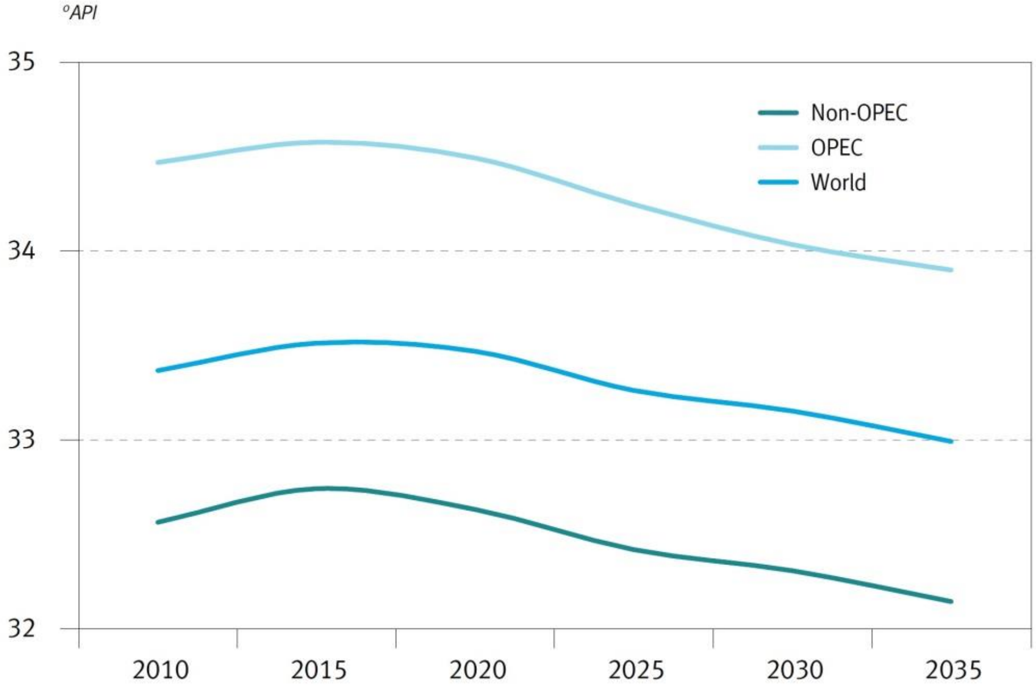


Figure 8 *Crude quality outlook in terms of API gravity (OPEC, 2011)*

However, it should be noted that actual sulfur content levels for products available in specific countries can differ from the ones permitted by regulators (OPEC, 2012).

(i) Gasoline quality specifications

Up-to-date petroleum product quality specifications lay stress upon the extensive use of gasoline with extremely low sulfur content. This tendency is especially noticeable in developed countries; nevertheless developing countries also expect nationwide penetration of low sulfur fuel.

This trend is particularly evident in developed countries, but it is now increasingly being adopted in the developing world too.

In the US the primary plan with its ultra-low sulfur gasoline program was to reduce sulfur to 80 ppm per gallon cap and 30 ppm annual average, as of 2004. Later, in 2010 US regulators have lowered the maximum standard to 30 ppm for all refineries, and California had set even lower specification at 15 ppm.

Since 2005, the EU refineries have produced certain quantities of 10 ppm gasoline together with 50 ppm fuels. As of January 2009, the situation has changed and the maximum allowable sulfur levels were further tightened to 10 ppm.

In China the sulfur limits are regulated on a regional basis. In the cities such as Shanghai, Guangzhou, Shenzhen, Dongguan and Nanjing the maximum sulfur level is set to 50 ppm, in Beijing it is set the strictest fuel quality requirement of 10 ppm, whereas the nationwide sulfur level is adjusted to 150 ppm in 2009. China is expected to lower its nationwide limits to 50 ppm by December 2013 and possibly to 10 ppm by 2016.

Similar tendency can be seen in India. Since 2010, 13 selected cities have lowered the sulfur content to 50 ppm, plus seven more cities since March 2012, whereas the nationwide sulfur gasoline level is 150 ppm. The Indian authorities made a list of 50 other cities with the big number of vehicles and high pollution, where it will be required to use the fuel with 50 ppm sulfur, and it is planned to be implemented by 2015.

Several other countries around the world are moving forward with lowering the maximum fuel sulfur content. This is particularly true in the Middle East, Russia, South Africa and some countries in Latin America. Saudi Arabia expects a nationwide penetration of 10 ppm gasoline by 2013, followed soon after by other countries in the Middle East region, while Russia plans to switch to 10 ppm gasoline by 2016. South Africa has agreed to enforce 10 ppm gasoline by 2017 (OPEC, 2011). Projected gasoline qualities in respect to sulfur content for 2012–2035 are shown in Table 3 (OPEC, 2011).

Table 3 *Expected regional gasoline sulfur content (OPEC, 2012)*

Region	2012	2015	2020	2025	2030	2035
US & Canada	30	30	10	10	10	10
Latin America	520	255	130	45	30	20
Europe	13	10	10	10	10	10
Middle East	605	235	75	25	16	10
FSU	315	115	35	20	12	10
Africa	795	493	245	165	95	65
Asia-Pacific	205	130	65	35	20	15

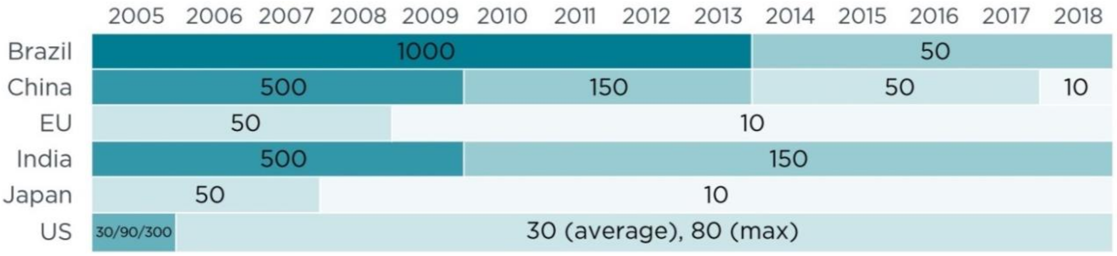


Figure 9 *Selected gasoline sulfur levels (ppm) in countries and regions around the world. Nationwide standards are shown; Brazil, China, and India have stricter fuel quality in some sub-national and municipal areas (ICCT, 2013)*

(ii) Diesel quality specifications

European Fuel Quality Directive has required the on-road and off-road diesel fuel sulfur content to be set at 10 ppm since 2011. Same maximum level of 10 ppm was legislated in Japan, Hong Kong, Australia, New Zealand, South Korea and Taiwan. A switch to 15 ppm for on- and off-road diesel was fully aligned in Canada since 2010. The same nationwide average level of 15 ppm came into effect in US in 2012, with the exceptions for small refineries, which are required to do so by 2014.

China planned to reduce its on-road diesel sulfur to 350 ppm in July 2012. This limit, however, is still not widely enforced. However, at the more regional level, Beijing has a diesel sulfur limit of 10 ppm, while cities of Shanghai, Guangzhou, Shenzhen, Dongguan and Nanjing have required a 50 ppm maximum since May 2012. India has also set two different diesel fuel specifications, one for nationwide supply and the other for 20 selected cities. The sulfur content specification for 20 urban centers is established at a 50 ppm maximum, and the national specification is 350 ppm. Other countries in Asia where improvements in on-road diesel quality have been observed include Indonesia, Malaysia, Philippines and Thailand.

In Latin America, the maximum sulfur limit for premium diesel in Argentina was set to 10 ppm in June 2011. Chile has required 50 ppm diesel since 2006. In other countries, such as Brazil, Ecuador and Mexico the progress has been reported, however the majority of Latin America has sulfur limits for diesel oil above 500 ppm.

Totally different situation do exist in Africa. The average sulfur content is in the range of 2,000 to 3,000 ppm for on-road diesel, and much higher for off-road. The only exception is South Africa, which plans a switch to 10 ppm fuels by 2017.

Table 4 *Expected regional on-road diesel sulfur content (OPEC, 2012)*

Region	2012	2015	2020	2025	2030	2035
US & Canada	15	15	15	10	10	10
Latin America	1,085	440	185	40	35	20
Europe	13	10	10	10	10	10
Middle East	1,725	415	155	70	20	10
FSU	440	175	60	15	10	10
Africa	3,810	2,035	930	420	175	95
Asia-Pacific	400	200	100	45	25	15

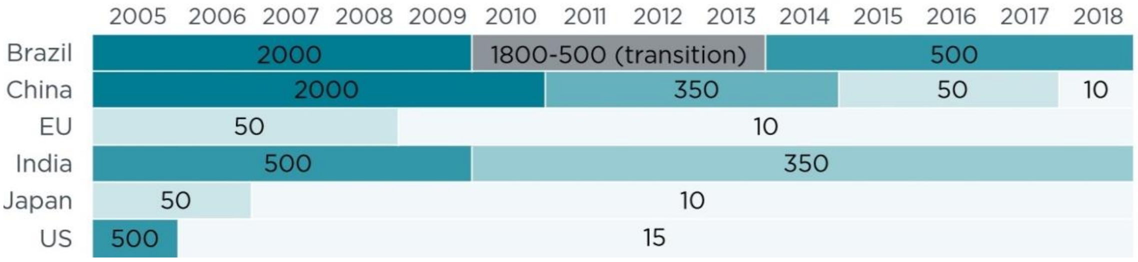


Figure 10 *Selected diesel fuel sulfur levels (ppm) in countries and regions around the world. Nationwide standards are shown; Brazil, China, and India have stricter fuel quality in some sub-national and municipal areas (ICCT, 2013)*

Table 4 summarizes regional diesel fuel qualities between 2012 and 2035 for on-road diesel, with a projected step-wise progress in quality improvements for all developing regions.

The authorities in Europe and North America already require ultra low sulfur level for on- and off-road fuel. The value is 15 ppm in North America and 10 ppm in Europe. By 2020, the most considerable reduction in sulfur content for on-road diesel compared to 2012 is projected to be in Latin America, the Middle East, and in FSU countries. With the exception of Africa, all regions are projected to reach an average on-road sulfur content of below 20 ppm by 2035 (OPEC, 2011).

(iii) Other products

In terms of other products, such as heating oil, jet kerosene and fuel oil, these are increasingly becoming targets for tighter requirements, especially in developed countries.

Sulfur content in Europe’s distillate-based heating oil was reduced from 2,000 ppm to 1,000 ppm in January 2008, and some countries, for example, Germany, provide tax incentives for 50 ppm heating oil to enable the use of cleaner and more efficient fuel burners. Parts of North America plan to reduce sulfur levels in heating oil to 15 ppm before 2020. Elsewhere, some progress is expected to be made in reducing the levels of sulfur in heating oil, but not to very low levels, and only after the transition in transportation fuels is completed (OPEC, 2011).

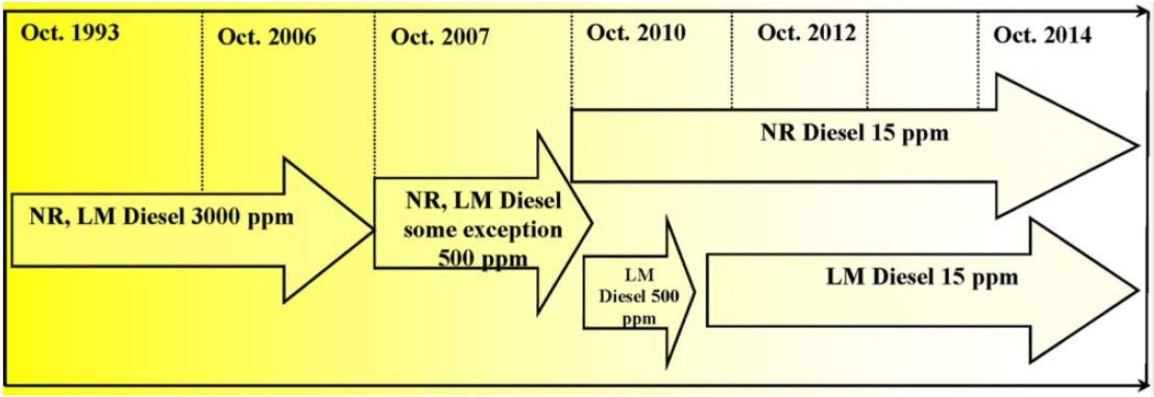


Figure 11 *Trends in sulfur specification for non-road diesel (NR, non-road and LM, locomotive and marine diesel) (Stanislaus et al., 2010)*

In Europe, reductions in the sulfur content of jet fuel have been discussed with initiatives aimed at global harmonization. However, no major progress has been achieved until now and, current jet fuel specifications still allow for sulfur content as high as 3,000 ppm, although market products run well below this limit, at approximately 1,000 ppm. Longer term, it is expected that jet fuel standards for sulfur content will be tightened to 350 ppm in industrialized regions by 2020, followed by other regions in 2025. Industrialized regions are also assumed to see a further reduction to 50 ppm by 2025 (OPEC, 2011).

Marine bunker fuels are also subject to regulation. As of January 2012, the global sulfur cap was lowered from 4.5% wt to 3.5% wt, and will be further lowered to 0.5% wt (5,000 ppm) as of January 2020. In September 2012, the European Parliament approved final legislation requiring all ships in the EU waters to switch to 0.5% wt sulfur fuel, or use corresponding technology allowing ships to reach the required emissions reduction, in 2020 (OPEC, 2011).

5. Challenges in production and processing

The studies on crude quality issues and up-to-date statistical data demonstrate all over again the relevance of the topic addressed. The quality of feedstock and crude slate is considerably deteriorating, becoming heavier and sourer (Figure 7-8). Commonly, the production and processing of high sulfur crudes and sour gases meet five major challenges, which have an effect on the development of energy efficient, low-cost technologies for separation units and to generally production schemes (Lepoutre, 2008).

Technical challenges

Crude oil and natural gas with high content of sulfur compounds claim complex and capital-intensive processes at all stages of production and handling, from upstream, through midstream to downstream segments of petroleum industry.

Technical challenges of development of high sulfur reservoirs are not defined directly. It differs from case to case. Nevertheless, there is a common challenge for almost all sour crude oil projects. This challenge is corrosion related problems. The corrosive environment is typically created when there is high content of H_2S and CO_2 combined with high pressure and high temperature. In such corrosive environment just a few materials can withstand. Moreover, because of high toxicity of the H_2S and the danger of metal failure as a result of stress corrosion cracking, extreme caution must be taken in selecting materials to drill and produce this type of energy source securely (Hamby, 1981). Causes of corrosion, corrosion control and mitigation tools will be described thoroughly in the following chapters.

Economic challenges

The next challenge is economic. It is linked to the high technical costs related to the production of sour crudes containing large amounts of acid gases. The size and the cost of process units and of acid gas handling facilities, such as H_2S transformation into sulfur units, shipping/storage of sulfur, compression, pumping or re-injection facilities, strongly dependent on the amount of feed stock.

Environmental challenges

The following challenge is environmental. Nowadays, the governments and environmental protection agencies have put limits on sulfur compounds in refined fuels. The tendency shows that one decade later the requirements will be much more stringent putting under the pressure oil and gas companies to develop more environmentally friendly technologies. To achieve this task significant amount of money has to be spent on research studies and process facilities.

Safety challenges

Production of sour oil and gas reserves with high content of hydrogen sulfide, leads to handle large quantities of this harmful gases. Hydrogen sulfide can be found in different states, the dense phase of it is precipitated in the acid gas facilities, and acid gas removal unit. Therefore, production and processing facilities is designed by taking account of sour gases, and it is particularly constrained by safety, because H_2S is highly toxic.

Sulfur marketing and environmental challenges

The last challenge is related to the sales of produced sulfur and its storage without harmful effect on the environment. Due to decreasing world demand for elemental sulfur, the economics of recovering sulfur from sour crude and natural gas has become unfavorable. The sulfur market is globally saturated. Even though, some companies are trying to find a solution for different utilization of sulfur, such as sulfur concrete, for instance.

5.1 Corrosion

Production, transportation and processing of crude oil and its following use as refined products and feedstock for chemicals claim a complex process. All of these processes are accompanied by various problems and corrosion is a major one, especially for the crude with high sulfur content. To date the annual cost of corrosion worldwide is estimated at over 3% of GDP of the planet, which is literally 3.3$ trillion. For that reason the problems related with corrosion is of extreme importance (Hays, 2013).

It is believed that corrosion should be controlled and mitigated at the early stage of indication. If not it can cause for the additional cost of lost time and involvement of employee, repair of equipment or replacement of whole construction. Without considering corrosion the outcome can be fatal (Nenry & Scott, 1994).

A detailed discussion of corrosion problems has been given by Henry and Scott (1994). Depending on where the corrosion occurs they divided corrosion into several groups, such as Corrosion in the Chemical Industry, Corrosion in Petroleum Production Operations, Corrosion in Petroleum Refining and Petrochemical Operations, and Corrosion of Petrochemical Pipelines. The corrosion caused by sulfur compounds is the following.

5.1.1 Corrosion in petroleum production operations

There are several environmental factors that are more or less relative to oil and gas production operations. The most important one is the environment found in actual reservoir formations. Corrosives encountered in those formations are carbon dioxide, hydrogen sulfide, polysulfides, organic acids, and sulfur in elemental state.

The first corrosion related problem is the presence of sulfate-reducing bacteria (SRB). SRB is in charge of the majority of the bacterial problems in oil production. It sours crude oil and gas leading to corrosion problems, also making it more difficult to refine environmentally friendly, high quality fuels. SRB produces volatile and toxic hydrogen sulfide as a by-product of respiration (Figure 12). The maximum allowable level of H_2S is set as low as 3 ppm, because sulfide concentrations even below 1 mg/l in the water phase may lead to high corrosion rates (Dunsmore, Evans, Jones, Burton, & Lappin-Scott, 2006).

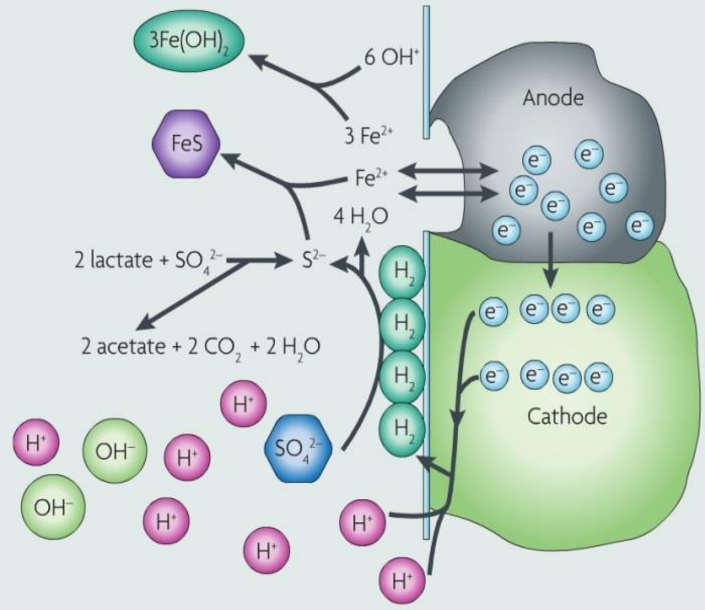


***Figure 12** Sulfate reducing bacteria and corrosion (Muyzer & Stams, 2008)*

Hydrogen sulfide is a relatively strong corrodent. When dissolved in water hydrogen sulfide is extremely corrosive as it becomes a source of hydrogen ions. In the absence of buffering ions, under 1 atmospheric H_2S partial pressure and pH level of 4, water is equilibrated. However, under very high pressure conditions, pH values as low as 3 have been calculated (Nenry & Scott, 1994).

Another corrosive property of H_2S is that it acts as a catalyst to promote absorption by steel of atomic hydrogen formed by the cathodic reduction of hydrogen ions. As a consequence, sulfide-stress cracking (SSC) takes a place. SSC can occur when H_2S is in contact with high-strength steel generally used in drilling, completing, and producing wells. SSC is a type of spontaneous brittle failure which occurs at stresses well below the yield strength of the material. Three conditions must be present for SSC to be present. The first is a surface tensile stress which can be both applied and residual. The second requirement is that the material must be exposed. The third requirement is that embrittling agent, hydrogen sulfide, must be present in the reservoir (Emerson, 2012).

Hydrogen sulfide also enters into a reaction with elemental sulfur. In a gas phase, sulfanes (free acid forms of a polysulfide) under high H_2S partial pressure can be formed so that elemental sulfur becomes mobile and is produced along with gaseous mixtures. Nevertheless, elemental sulfur starts to precipitate as a result of pressure reduction in the upper part of production tubing, which causes sulfur plugging (Nenry & Scott, 1994).

5.1.2 Corrosion in petroleum refining and petrochemical operations

The major corrosion problems in oil and gas processing facilities are not caused by hydrocarbons but by various inorganic compounds, such as water, hydrogen sulfide, hydrofluoric acid, and caustic. There are two essential sources of these conglomerates: feed-stock contaminants and process chemicals, including solvents, neutralizers, and catalysts (Nenry & Scott, 1994).

For practical purposes, corrosion in petroleum refineries and petrochemical plants is classified as low- and high-temperature corrosion. Low-temperature corrosion is considered to take place at temperatures below $260^{\circ}C$ in the presence of water. The main source of low-temperature corrosion is the contaminants in crude oil. Those contaminants are water, hydrogen sulfide, hydrogen chloride, nitrogen compounds and polythionic acids (API, 1973).

Crude oils and gases that contain hydrogen sulfide are processed by most refineries (Hudjins, 1969). Hydrogen sulfide is also can be found in some feed stocks handled by petrochemical plants. This harmful chemical compound forms the black sulfide film seen in almost all refinery equipment (Ewing, 1955). Hydrogen sulfide is the main component of refinery sour waters and can cause corrosion problems in overhead systems of fractionation towers, in hydrocracker and hydrotreater effluent streams, in catalytic cracking units, in sour water stripping units, and, of course, in sulfur recovery units (Piehl, 1968).

Sulfur compounds include hydrogen sulfide, polysulfides, mercaptans, aliphatic sulfides, and thiophenes. Those contaminants, excluding thiophenes, react with metal surfaces at high temperatures forming metal sulfides, organic molecules, and hydrogen sulfide. The corrosiveness of sulfur compounds increases with accumulating temperature. Depending on a specific process, corrosion can be in the form of uniform thinning, localized attack, or erosion-corrosion (Nenry & Scott, 1994).

When it comes to high-temperature processes, corrosion is of considerable importance. Facility failures can have undesirable consequences because refinery processes at high temperatures involve high pressures as well. With crude oil streams, there is always the danger of fire when ruptures take place. That is why corrosion by different sulfur compounds at temperatures between 260 and 540˚C is a general issue in petroleum refining and petrochemical processes (Nenry & Scott, 1994).

5.2 Corrosion control mechanisms in sour systems

There are considerable numbers of corrosion detection methods. Two parameters, such as the operating conditions and chemical nature of the reservoir fluid have to be known in order to select corrosion control method properly. The correct observation and analytical solutions are also important. After necessary studies and considering pros and cons of the available control methods corrosion detection system should be chosen. The major currently available methods are given in Table 5 below, but it should be noted that there are other methods as well, such as iron and manganese counts, galvanic meters, electromagnetic flux leakage, chemical and bacteria analysis, metallurgical examination of failed equipment, simulation studies, and operating condition monitoring.

Table 5 *Corrosion control mechanisms in sour systems (Gerus, 1974)*

Weight loss coupons	*Advantages:*	*Disadvantages:*
Weight loss coupons are metal strips that are located into actual flow stream and allowed to corrode spontaneously. The coupons are scaled before installation. After some time of being in the fluid stream it is cleaned and scaled again before removal. The corrosion rate is defined by weight loss, exposure time, the dimensions of the coupon, and is measured in mm/year or g/cm^2.	•It is cheap and it does not require significant engineering maintenance.	•The relatively infrequent data is obtained; •Coupons placed on the upper part will not detect severe corrosion, as in most gathering facilities the corrosion phenomena is limited to the bottom area of the pipe wall; •Coupons in short term observation periods cannot indicate corrosion rate.
Radiography	*Advantages*	*Disadvantages*
Radiography is the extensively used corrosion control method. The general concept of the method is to place radioactive source on one side of a pipe and to put radiographic film on the other side, and to allow the radioactive emissions to pass through the metal. The X-ray absorption is proportional to the mass of metal that the rays pass through. Hence, the exposed film indicates pits in the pipe as dark spots.	•The actual pictorial representation of the interior of the pipe; •The inspection is held without interrupting of whole process; •The radiography is the only method which detects pitting type corrosion.	•Only specific locations can be observed; •The earth around the pipe is removed at a certain locations.
Ultrasonic inspections	*Advantages*	*Disadvantages*
Ultrasonic inspections are used to measure wall thickness by means of sound waves. The instrument consists of transducer probe which is connected to digital recording tool. The transducer transmits sound waves through the metal and receives the reflected signal.	•The large number of inspections can be made in a relatively short time; •The instrument is portable and can be used any place; •The measurements can be made without stopping the flow line.	•The extreme localization of inspection; •The shape of the corroded surface affects the sound wave reflection.
Visual inspections	*Advantages*	*Disadvantages*
Visual inspections by experienced worker are one of the most efficient methods identifying corrosion problems. While using this method pit depths can be	•Any pit depth can be measured and a pitting corrosion rate can be established; •Excellent for close observation	•Extreme localization of inspection; •Expensive for the installation of valves and bypass loops at

measured and the remaining life of the components of process facilities can be estimated.	of severely corrosive locations.	every location.
Hydrogen probe	*Advantages*	*Disadvantages*
Hydrogen probes detect the level of corrosion affected by hydrogen sulfide. The concept of the method is that atomic hydrogen diffuses through the metal probe and combines in the cavity to form hydrogen gas. The rate of gas formation detected by pressure increases within the sample and this rate is related to corrosion rate in the system.	•Fluid stream is uninterrupted	•Qualitative rather than quantitative indications •The high sensitivity of the instrument

5.3 Corrosion mitigation techniques in sour systems

Mitigation of corrosion is considered to be the final step in corrosion problems in sour systems. First of all, corrosion mechanisms should be defined and then mitigation tool is decided upon. After detection of specific corrosion mechanism, more detailed studies can be carried out, and after that the mitigation techniques can be chosen. There are a lot of mitigation techniques which is used in sour systems and following are the major ones (Gerus, 1974):

(i) Scraping and pigging

Figure 13 *Corrosion control by scraping and pigging (O'Meara, 2006)*

The technique of using scraping is based on removal of scale, corrosion products and other compounds from the surface of pipe wall. The scraper is a cylindrical tool with a diameter a little greater than the internal diameter of the pipe and with wire brushes and metal discs (Figure 13). Pigging is performed in the same way as scraping, but the device does not have scraping brushes or plates. The pig is usually placed in gathering line, and then propelled through the system, commonly by well pressure. The disadvantage of the method is that pig launching and receiving facilities must be installed through all gathering system.

(ii) Chemical cleaning

Chemical cleaning is the injection of specific chemicals into the system for the purpose of dissolution of deposit or slug. Following removal of the solution results in clean pipe surface. Often, this method is used in combination with pigging after dissolution process is completed. The chemical cleaning is an efficient method; however, as the chemical used can react with the iron in the pipe, precautions should be taken.

(i) Corrosion inhibitors

Corrosion inhibitors injection is the mostly implemented technique to the mitigation sour oil and gas corrosion. Corrosion inhibitors are the compounds that, when introduced to the system, reduces the metal loss due to corrosion attack. These inhibitors can interfere with the anodic or cathodic reaction, moreover, can form protective barrier on the metal surface as it is shown in Figure 14. The dosage and frequency of treatment are dependent on different factors, including severity of corrosion, total amount of fluid produced, percentage of water, nature of corrodent, chemical selected, and fluid level in the casing annulus (Nenry & Scott, 1994).

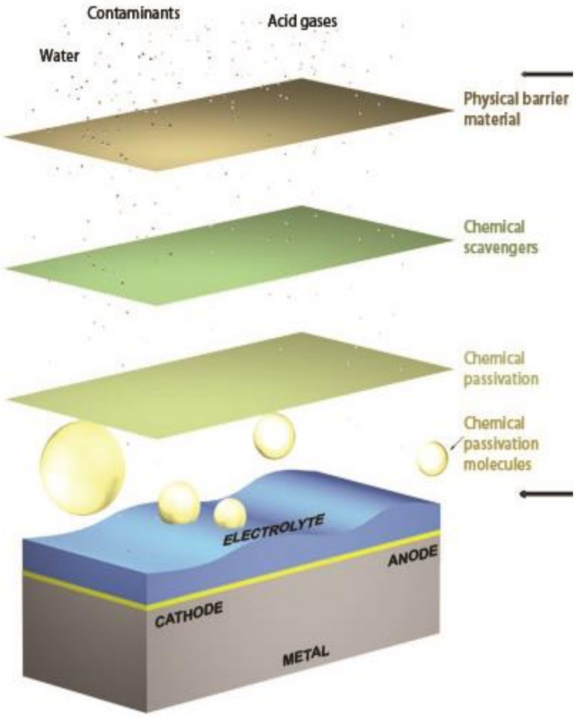


***Figure 14** Corrosion mitigation by inhibitors (ICT, 2013)*

(ii) Dew point control

Corrosion does not occur if there is no complete electrical circuit from anode to cathode. Brine water commonly provides an electrical environment in the produced fluid. So for, if the system with sour content is maintained without water or condensation the occurrence of corrosion becomes insignificant. The system which does not produce water can be protected from water or condensation by controlling the dew point temperature. The dew point temperature can be accomplished by adding thermal energy to the system.

(iii) Biocides

The introduction of biocides into a system is right when the corrosion mechanism has been proved to be biologically induced. They are added into the system to kill the bacteria upon contacts. This results on termination of the corrosive attack on the surface.

(iv) Internal coatings and linings

This method of corrosion mitigation is extremely effective as it helps to isolate the corrosive fluid form the metal surface. The success is achieved by using coatings and linings. The coatings provide a barrier to the diffusion of reactants and the flow of electrical current. As a result, corrosion is avoided. By means coatings can be permanent and temporary. The first one is a thin sheet of corrosion resistant metal or alloy to a thicker base metal at elevated temperatures. Coatings can be formed and fabricated into transportation and process facilities. The second one is applied by the automatic machine that cleans the pipe or by hand sprayers.

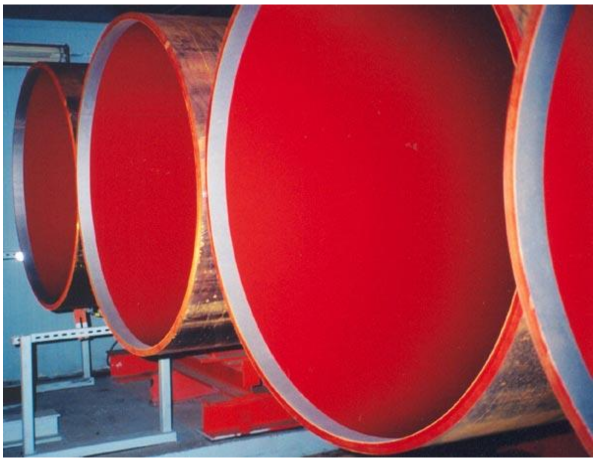


Figure 15 *Typical coated steel pipe (Offshore Technology, 2012)*

6. Petroleum products

6.1 Classification of petroleum products

The assortment of petroleum-refining industry consists of more than 500 types of gaseous, liquid and solid petroleum products in terms of their purpose. Consequently, products are difficult to place on an individual evolutionary scale. However, they can be classified in a wide variety of different ways within the oil industry (Favennec, 2001):

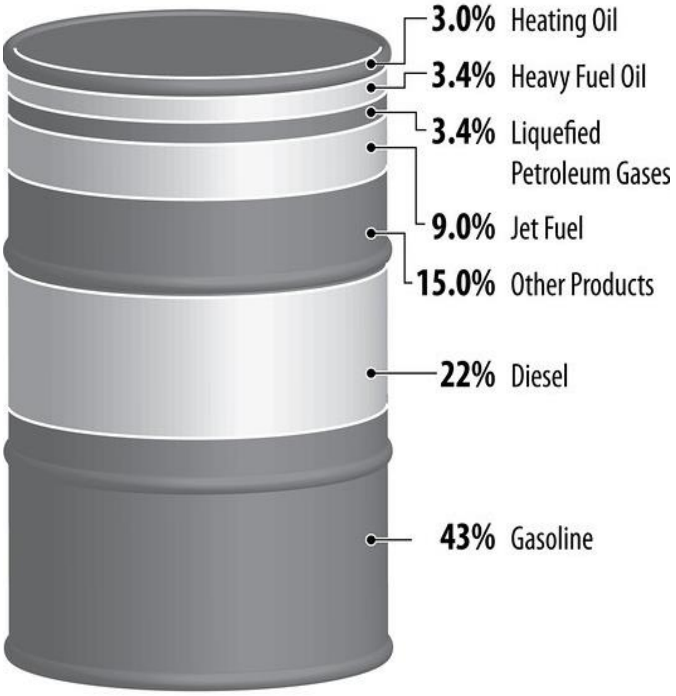


Figure 16 *Typical product produced from a barrel of oil in US (EIA, 2012)*

- Refinery operators differentiate between light products (gas and gasolines), middle distillates (kerosene, automotive gas oil and heating gas oil), and heavy products (heavy fuel oil and bitumen).
- For transportation purposes, products are distinguished as white products (motor gasoline, jet fuel, and automotive and heating gas oil) and black products (fuel oil and bitumen).
- Product dealers ascertain between main products and specialties. Main products are sold in a large quantities and distinction is confined so the product assortment is not considerable. Margins for main products, such as motor fuels, jet fuel, heating gas oil and heavy fuel oil, are fairly low. For sales of specialties, such as LPG, aviation gasoline, lubricants and bitumen, there is an opposite situation. They are sold in a little volume but give a high added value, both in terms of the products itself or the service provided.

7. Composition of crude oils and petroleum products

Crude oil is a unique mixture of a great number of individual chemical compounds. Each crude oil has a compound which is not matched exactly in composition or in properties by any other sample of crude oil. Chemical and physical composition of crude oil can vary not only with the location and age of the oil field, but also with the depth of the individual well. More than that, two neighboring wells may produce hydrocarbons with considerably different characteristics.

In order to understand the nature of sulfur compounds in crude oil the basic knowledge of general crude composition is needed. The main constituents present in crude oils are hydrocarbons. The hydrocarbon content may be as high as 97% by weight in light paraffinic oils or as low as 50% by weight in heavy crude and bitumen. Other non-hydrocarbon constituents include small amount of organic compounds containing sulfur, oxygen, and nitrogen, as well as compounds containing metallic elements, such as vanadium, nickel, iron, and copper (Speight, 2007). Sulfur compounds are the focus in this master thesis and will be discussed in more detail throughout subsequent chapters.

7.1 Hydrocarbon compounds

(i) Saturated Aliphatic Hydrocarbons or Alkanes or Paraffins

Alkanes are straight-chain normal alkanes and branched iso-alkanes with the general formula C_nH_{2n+2}. Alkanes are present in all crude oils. Usually, the alkane content in the oils ranges from 20 to 50%. In waxy crudes content of alkanes can be as high as 60% or even more, conversely, in low-paraffinic oils the alkane content may fall to 1.2%. If the distribution of alkanes by fractions is considered, then there is the following general pattern for all crudes: the content of alkanes decreases with increasing boiling point of petroleum fractions (Ryabov, 2009).

(i) Saturated Cyclic Hydrocarbons or Cycloparaffins or Napthenes or Cycloalkanes

Saturated cyclic hydrocarbons make up the bulk of petroleum hydrocarbons. The cycloalkane composition in crude worldwide typically varies from 40 to 70%. The content of these hydrocarbons in some naphthenic oils can sometimes reach 80%. The distribution of cycloalkanes is essentially equal for all petroleum fractions.

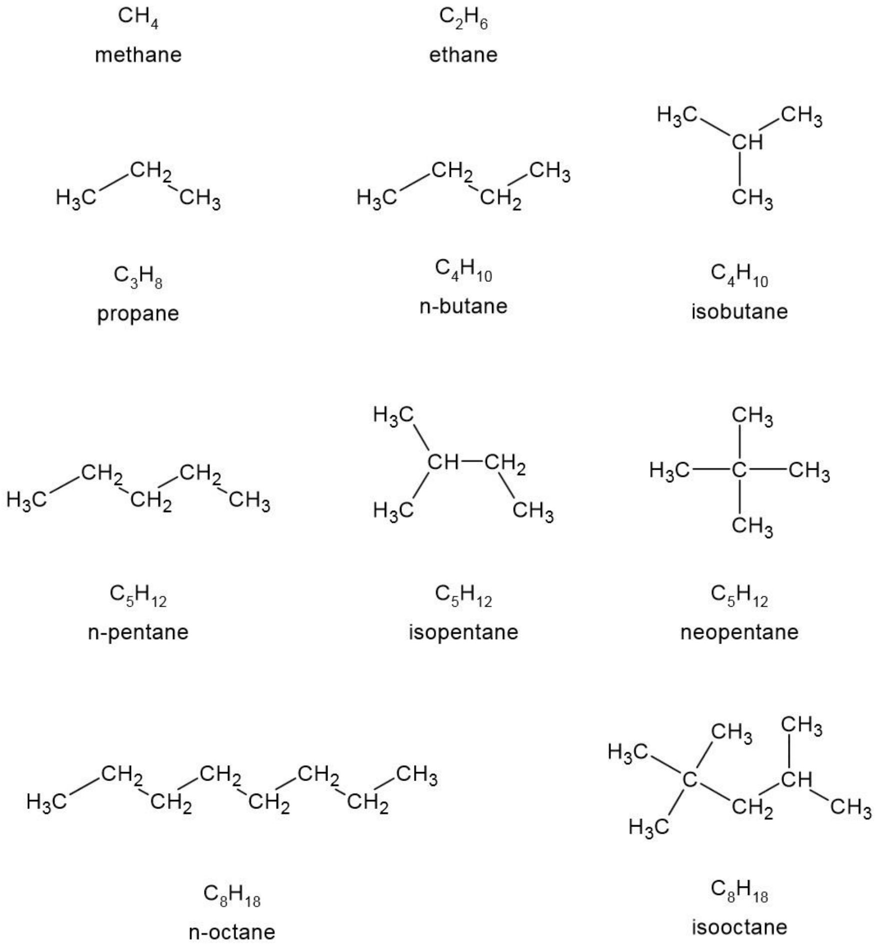


Figure 17 *Isomers of selected paraffins (Robinson, 2013)*

Although the study on chemical composition of napthenes continues for more than 100 years, those hydrocarbons, especially in high petroleum cuts, are the least understood hydrocarbons in crude oils. This is due to the complexity of their composition conditioned by a variety of isomers (Ryabov, 2009).

(ii) Aromatic Hydrocarbons

Aromatic hydrocarbons in crude oil are presented by monocyclic and polyunsaturated hydrocarbons. The content of aromatics normally ranges from 15 to 20%; in aromatic-base crude oil their content can reach as high as 35% (Ryabov, 2009). The presence in their structure of at least one ring containing double bonds significantly influences on their chemical properties. Aromatic hydrocarbons, such as benzene, toluene, and xylenes, are primary raw materials for the petrochemical industry, moreover, they largely contributes to the octane number of gasoline. However, the negative properties of higher homologs, such as environmental and public health problems and degradation of the catalyst activity, are also known (Wauquier, 1995).

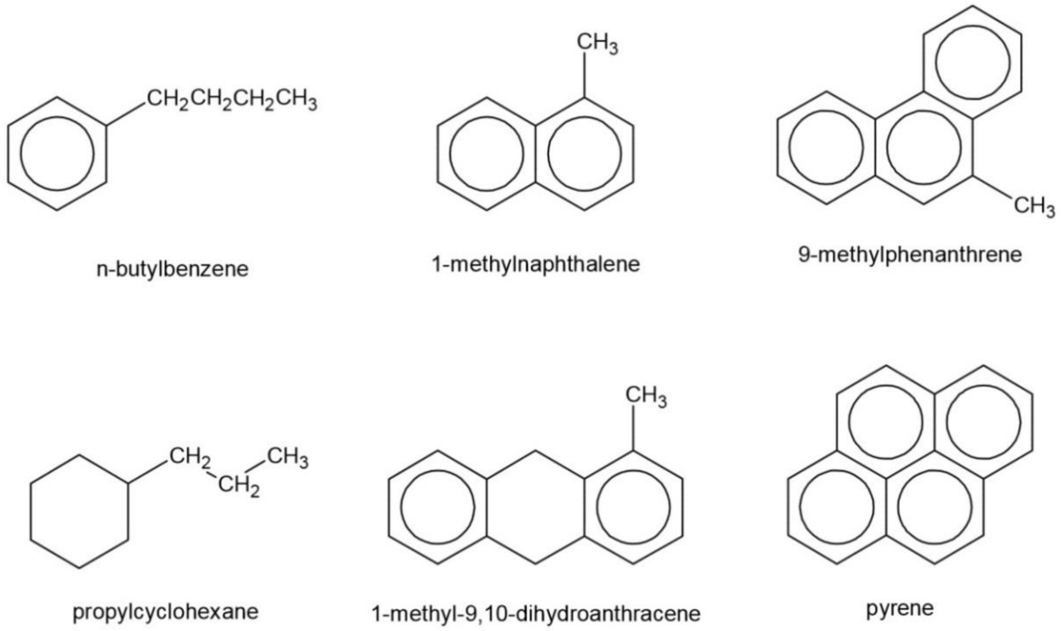
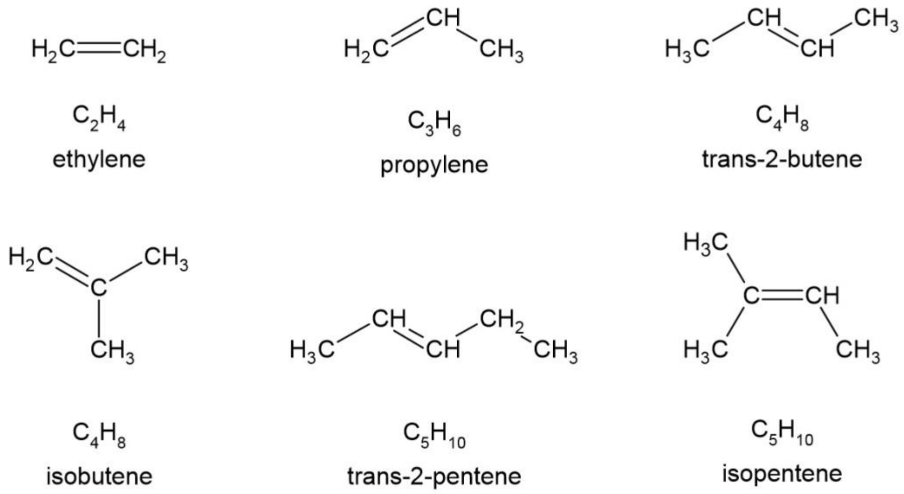


Figure 18 *Aromatics and napthenes found in crude oil (Robinson, 2013)*

(iii) Unsaturated Aliphatic Hydrocarbons or Olefins or Alkenes

The presence of olefins in crude oil has been under dispute for many years. However, evidence for the presence of significant proportions of olefins in Pennsylvanian crudes has been obtained (Speight, 2007). Next evidence is found in East Siberian and Tatar crude oils where the content of olefins can be in range of 15-20% (Ryabov, 2009). Even though, those findings are assumed as a few special cases.

In spite of previous facts, olefins are found in refining products, especially in the fractions coming from conversion of heavy fractions. The first few substances of these chemical compounds are very important feedstock materials for petrochemical industry: ethylene, propylene, and butenes (Wauquier, 1995). Selected light olefins are presented in Figure 19.



C_2H_4 ethylene

C_3H_6 propylene

C_4H_8 trans-2-butene

C_4H_8 isobutene

C_5H_{10} trans-2-pentene

C_5H_{10} isopentene

Figure 19 *Selected light olefins (Robinson, 2013)*

7.2 Non–Hydrocarbon compounds

(i) Heteroatomic Organic Compounds

Crude oils contain considerable amounts of organic non-hydrocarbon constituents. Those constituents when present in organic compounds, atoms other than carbon and hydrogen are called hetero-atoms. Sulfur-, nitrogen-, oxygen- containing compounds (Figure 20) appear throughout the entire boiling range, but tend to concentrate mainly in the heavier fractions (Speight, The Refinery of the Future, 2011).

Although they are minor constituents of crude oil, their influence on processing costs can be major. Some of the sulfur and nitrogen compounds that present problems to oil refiners. When burned in vehicles or power plants, high-sulfur fuels cause acid rain. For many refining processes, sulfur is a catalyst poison. Nitrogen is also catalyst poison. Therefore, refiners devote a considerable amount of time and money to remove hetero-atoms from intermediate streams and finished products.

(i) Organometallic compounds

In the heaviest fractions such as resins and asphaltenes organometallic compounds such as nickel and vanadium are found and their concentrations have to be reduced to convert the oil to transportation fuel. The level of metal compounds ranges from few parts per million to 200 ppm for nickel and up to 1200 ppm for vanadium.

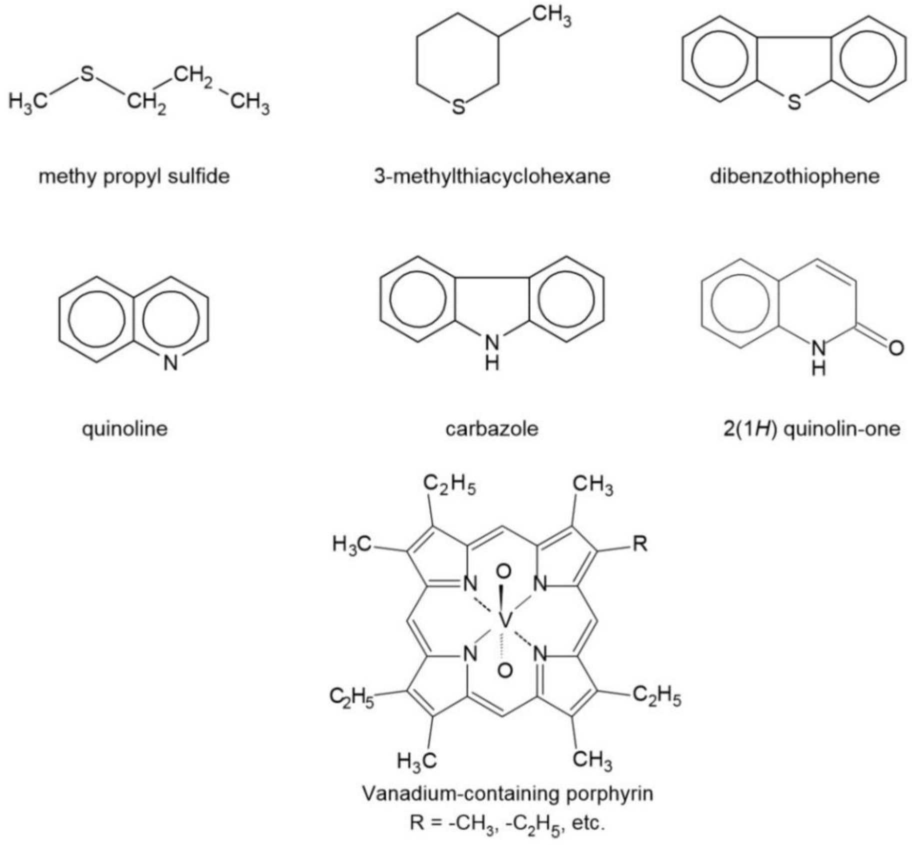


Figure 20 *Hetero-atom compounds found in crude oil (Robinson, 2013)*

8. Sulfur content of crude oils

8.1 Origin of sulfur

Sulfur in crude oil comes generally from the decomposition of organic matter, and with the passage of time and of gradual settling into strata, the sulfur segregates from crude oil in the form of hydrogen sulfide that appears in the associated gas, some portion of sulfur stays with the liquid. Another theory behind origin of sulfur compounds is the reduction of sulfates by hydrogen by bacterial action of the type desulforibrio desulfuricans:

$$4H_2 + SO_4^{=(\text{bacteria})} \rightarrow H_2S + 2OH^- + 2H_2O$$

Hydrogen comes from the reservoir fluid and the sulfate ions are kept in the reservoir rock, as a result hydrogen sulfide is generated. The H_2S formed can react with the sulfates or rock to form sulfur that remains in composition of crude as in the case of oil from Goldsmith, Texas, USA. Moreover, under the conditions of pressure, temperature and period of formation of the reservoir H_2S can react with the hydrocarbons to give sulfur compounds (Wauquier, 1995):

$$3H_2S + SO_4 \rightarrow 4S + 2OH^- + 2H_2O$$

Sulfur compounds are among the most important non-hydrocarbon heteroatomic constituents of petroleum. There are significant amount of sulfur species found in crude oil and sulfur compounds of one type or another are present in all crude oils. Furthermore, only preferred type of sulfur exist in any particular crude oil, and this is dictated by the prevailing conditions during the formation, maturation, and even in situ alteration.

In general, the higher the density of the crude oil, the lower the API gravity of the crude and the higher the sulfur content. The total sulfur in crude oil can vary from 0.04% w/w for light crude oil to about 5% w/w for heavy crude oil and tar sand bitumen. Nevertheless, the sulfur content of crude oils which is produced from different locations varies with time, depending on the chemical composition of newly discovered fields, especially those in different geological environments (Speight, 2007).

8.2 Nature of sulfur compounds

Sulfur compounds are substances of different chemical nature, from the elemental sulfur to hydrogen sulfide and mercaptan compounds, sulfides, open-chain and cyclic disulfides, and heterocyclic derivatives of thiophene, thiophane and other more complex compounds. To date, with the exception of low molecular weight compounds, most of the sulfur compounds oils are not deciphered. Free elemental sulfur is rarely found in crude oils. The emergence of free sulfur is associated with the decomposition of more complex sulfur compounds.

The bulk of sulfur compounds found in crude oil are distributed between the heavy cuts and residues (Table 7) in the form sulfur compounds of the napthenophenanthrene or naphthenoanthracene type, or in the form of benzothiophenes, that is molecules having one or several naphthenic and aromatic rings that usually contain a single sulfur atom (Wauquier, 1995).

Table 6 *Sulfur content of selected crude oils (surface conditions) (Wauquier, 1995)*

Crude oil name	Country of origin	Weight % sulfur
Bu Attifel	Libya	0.10
Arjuna	Indonesia	0.12
Bonny light	Nigeria	0.13
Hassi Messaoud	Algeria	0.14
Ekofisk	North Sea (Norway)	0.18
Arabian light	Saudi Arabia	1.80
Kirkuk	Iraq	1.95
Kuwait	Kuwait	2.50
Cyrus	Iran	3.48
Boscan	Venezuela	5.40

Table 7 *Distribution of total sulfur in the different cuts of crude Arabian light (Wauquier, 1995)*

Cut	Light gasoline	Heavy gasoline	Kerosene	Gas oil	Residue	Crude
Temperature interval, ˚C	20-70	70-180	180-260	260-370	370+	-

Specific gravity, d_4^{15}	0.648	0.741	0.801	0.856	0.957	-
Average molecular weight	75	117	175	255	400	-
Total sulfur, weight %	0.024	0.032	0.202	1.436	3.167	1.80
Number of moles of sulfides/Total number of moles	1/1800	1/855	1/90	1/9	1/2.5	-

The sulfur compounds determined in crude oil are classified into six chemical groups.

(i) Free elemental sulfur S

Free elemental sulfur is rarely found in crude oil; however it can be present in a suspension or dissolved in the liquid. Sulfur, while crude oil is heated, partially reacts with hydrocarbons:

$$2RH+2S \rightarrow R-S-R+H_2S \qquad (X)$$

It is believed that determination of the presence of elemental sulfur in oil is a complex process and that any declaration of its presence has met with lack of confidence (Eccleston et al., 1992). The crude oil from Goldsmith, which is in Texas, is richest in elemental sulfur (1% by weight for a total sulfur content of 2.17%) (Wauquier, 1995).

(ii) Hydrogen sulfide H_2S

Hydrogen sulfide is a colorless, flammable, harmful gas that smells like rotten eggs (NPI, 2013). H_2S is found in reservoir gas and dissolved in the reservoir liquid (<50 ppm by weight). Often the appearance of H_2S in petroleum fractions is a consequence of thermal decomposition of organosulfur compounds (Ryabov, 2009). It is itself and the sulfur dioxide (SO_2), the product of H_2S combustion cause poisoning of humans, animals and plants.

The presence of H_2S in the reservoir crude determines the number of serious complications for production of oil, due to its high corrosiveness and toxicity. It causes corrosion of steel pipes and tanks, compressors, fittings and other surface equipment, particularly in the presence of carbon dioxide and water vapor in the feed, and under elevated temperatures. Therefore, the gas used as a fuel in industrial furnaces must not contain hydrogen sulfide above the limit determined in each individual case. Furthermore, the presence of H_2S accelerates the formation of gas hydrates.

H_2S is mostly formed during processing operations such as catalytic cracking, hydrodesulphurization, thermal cracking and by thermal decomposition during distillation (Wauquier, 1995).

(iii) Thiols

Thiols or mercaptans are organosulfur compounds that contain a sulfhydryl group (SH), also known as a thiol group, that is composed of a sulfur atom and a hydrogen atom attached to a carbon atom. This molecular structure is what distinguishes thiols from other organic chemical compounds with an oxygen-to-carbon bond configuration. It is also what gives many high velocity thiols a persistent and highly unpleasant odor that is reminiscent of rotten eggs (Mayer, 2013).

The general formula of thiols is R – S – H, where R stands for an aliphatic or cyclic radical. S – H group is responsible for their acidic behavior. The level of thiols in crude oil is very low, if not zero. However, they may appear from other organosulfur compounds during refining operations, which is illustrated in Table 9. It should be noted that the content of mercaptans in crude varies from 0.1 to 15 % mass from total content of sulfur compounds (Ryabov, 2009).

Table 8 *Distribution of mercaptan sulfur among the different cuts of Arabian light crude oil (Wauquier, 1995)*

Nature of cut (temperature interval, ˚C)	Mercaptan sulfur, %	Total sulfur, %	% mercaptan sulfur
			total sulfur
Crude petroleum	0,0110	1,8	0,6
Butane	0,0228	0,0228	100
Light gasoline (20-70˚C)	0,0196	0,0240	82
Heavy gasoline (70-150˚C)	0,0162	0,026	62
Naphtha (150-190˚C)	0,0084	0,059	14
Kerosene (190-250˚C)	0,0015	0,17	0,9
Gas oil (250-370˚C)	0,0010	1,40	<0,1
Residue (370 $^{+}$˚C)	0	3,17	0

***Table 9** Mercaptans identified in crude oils (Wauquier, 1995)*

Name	Chemical formula	Boiling point, ℃	Cut
Methanethiol	CH_4S	6	Butane Gasoline
Ethanethiol	C_2H_6S	34	Gasoline
2 methylpropanethiol	$C_4H_{10}S$	85	Gasoline
2 methylheptanethiol	$C_8H_{18}S$	186	Kerosene
Cyclohexanethiol	$C_6H_{12}S$	159	Gasoline

(iv) Sulfides

The sulfides are organosulfur compounds which can have a linear or ring structure. They are chemically neutral. The boiling points of sulfides are higher than of mercaptans for molecules of equal carbon number. Examples of sulfides identified in selected crude oils are shown in Table 10. They create the bulk of sulfur containing hydrocarbons in the middle distillates (kerosene and gas oil), where their content is equal to 50-80% of total sulfur compounds (Ryabov, 2009).

***Table 10** Sulfides identified in the crude oils (Wauquier, 1995)*

Name	Chemical formula	Boiling point, ℃	Cut
3 Thiapentane	$C_4H_{10}S$	92	Gasoline
2 Methyl – 3 thiapentane	$C_5H_{12}S$	108	Gasoline
Thiacyclohexane	$C_5H_{10}S$	141,8	Gasoline
2 Methylthiacyclo-pentane	$C_5H_{10}S$	133	Gasoline
Thiaindane	$C_7H_{12}S$	235,6	Kerosene
Thiabicyclooctane	$C_7H_{12}S$	194,5	Kerosene and gas oil

(v) Disulfides

The disulfides (general formula: R – S – S – R’) are found in small quantities in petroleum fractions with a boiling point up to 300˚C. They account for 7-15% of the total sulfur (Ryabov, 2009).

The disulfides are complex chemical compounds which are difficult to separate; as a result, few have been identified:

Dimethyl disulfide (2,3 dithiobutane)

$CH_3 – S – S – CH_3$

Diethyl disulfide (2,3 dithiohexane)

$CH_3 – CH_3 – S – S – CH_2 – CH_3$

(vi) Thiophene and derivatives

Thiophene and its derivatives are neutral cyclic and temperature resistant compounds with five-membered ring. They do not dissolve in water, and their chemical properties are similar to aromatic hydrocarbons.

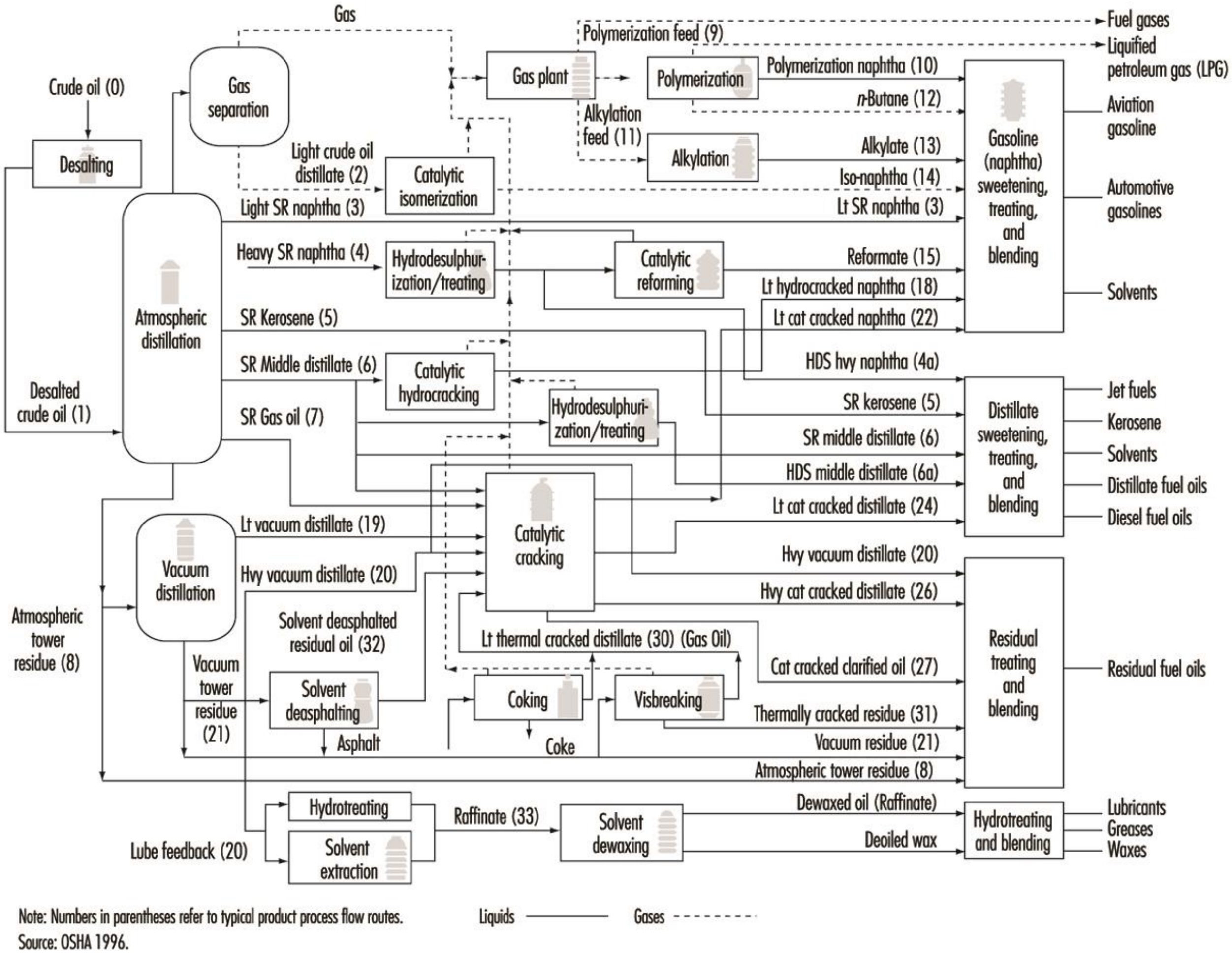
The first determination of thiophene and its derivatives was in 1899, and it was believed that they came from the degradation of sulfides during refining operations. That was until 1953, the year when the methyl-thiophenes were identified in kerosene from Agha Jari crude oil, Iran. The existence of those sulfur compounds was no longer doubted after the identification of benzothiophenes and their derivatives (Table 11).

Table 11 *Thiophene derivatives identified in crude oils (Wauquier, 1995)*

Name	Chemical formula	Boiling point, ℃	Cut
Thiophene	C_4H_4S	84	Gasoline
Dimethylthiophene	C_6H_8S	141.6	Gasoline and Kerosene
Benzothiophene	C_8H_6S	219.9	Kerosene
Dibenzothiophene	$C_{12}H_8S$	300	Gas oil

9. Fundamentals of refinery processing

Petroleum refineries are extensive, continuous flow industrial process plants which involves considerable capital expenditures. The crude oil is processed and refined into more used products such as petroleum naphtha, gasoline, diesel fuel, jet fuel, liquefied petroleum gas, petrochemical feedstocks, home heating oil, fuel oil, asphalt and others. Those transformations occur in a virtue of various physical and chemical processes proceeding in system units by separating feed into different petroleum fractions depending on their boiling range and carbon number distribution, and refining these fractions into finished products, afterwards (MathProInc., 2011). The overview of refining processes and operations are given in Figure 21 and Table 25.



Note: Numbers in parentheses refer to typical product process flow routes.

Source: OSHA 1996.

Figure 21 *Overview of refining processes and operations* (Kraus, 2011)

9.1 Classifying refineries by configuration and complexity

All refineries are unique. Their configuration and complexity differ from one refinery to another one. They have different histories, locations, preferred crude oil slate, quality specifications for refined products and market drivers. For that reason, there is no distinct classification which can group all of the possible combinations and permutations of the processes that fit together. Although no two refineries have identical configurations, they can be classified into groups of comparable refineries, defined by refinery complexity (Fahim et al., 2010):

- Simple refinery. It has atmospheric crude distillation, a catalytic reformer to produce high octane gasoline, and middle distillate hydrotreating units.
- Complex refinery. It has in addition to the units of a simple refinery, conversion units such as hydrocrackers and fluid catalytic cracking units.
- Ultra-complex refinery. The refinery has all of the units above in addition to deep conversion units which convert atmospheric or vacuum residue into light products.

The complexity of a refinery can be assessed by calculating the complexity factor. Each unit has a coefficient of complexity (CC_i) defined as the ratio of the capital cost of this unit per ton of feedstock to the capital cost of the crude distillation unit (CDU) per ton of feedstock. The complexity factor (CF_i) of the whole refinery is then calculated from the coefficients of complexity for the units in the refinery as follows:

$$CF = \sum_{i}^{N} \frac{F_i}{F_{CDU}} CC_i$$

where, F_i and F_{CDU} are the feed rate to unit i and CDU, respectively.

10. Classification of desulphurization technologies

There is no unique way of classifying the desulphurization processes. They can be categorized by the type of sulfur compound being removed, the role of hydrogen, or the nature of process used.

Crude oil desulphurization technologies can be grouped based on the nature of a key process to remove sulfur (Figure 22). First type of classification refers to the most studied and commercialized catalytic technologies, which include conventional HDS, HDS by advanced catalysts and/or by advanced reactor design, and HDS with additional chemical processes to meet the fuel specifications.

Second class of desulphurization is based on the physico-chemical processes which vary in nature from catalytic processes, including distillation, alkylation, oxidation, extraction, adsorption or combined version of these processes (Babich & Moulijn, 2003).

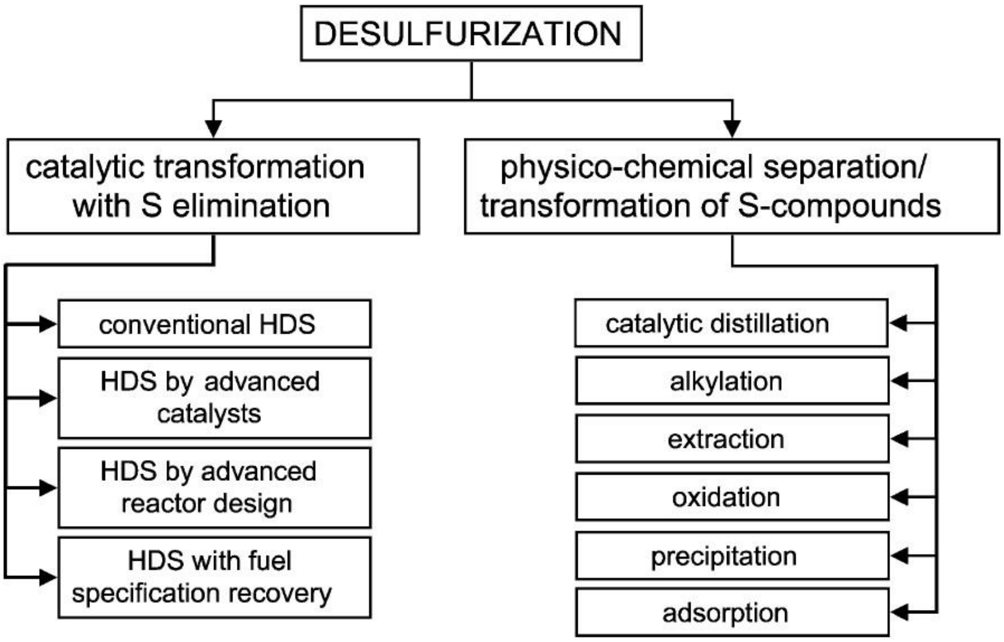


Figure 22 *Desulphurization technologies classified by nature of a key process to remove sulfur (Babich & Moulijn, 2003)*

11. *Hydrotreating*

Hydrotreating is a refining process in which the feedstock is treated at temperature and under pressure where thermal decomposition in the presence of hydrogen is minimized. The main purpose is to remove about 90% of undesirable contaminants including nitrogen, sulfur, oxygen, metals, and unsaturated hydrocarbons (olefins) from liquid petroleum fractions. Hydrotreating processes have been developed in connection with the increase of high sulfur heavy crude refining and more stringent quality requirements for fuels and feedstocks for catalytic processes.

Generally, hydrotreating is applied prior to processes, such as catalytic reforming and catalytic cracking so that the catalyst is not contaminated by unrefined feedstock and that organosulfur compounds are removed and middle-distillate fractions are converted into finished products such as kerosene, diesel and heating fuel oils. Furthermore, hydrogenation processes converts olefins and aromatics into aromatic compounds.

There are several important reasons for removing heteroatoms from petroleum fractions and some of them are listed below (Speight, 2007):

1. Corrosion control and mitigation while refining, handling, or use of different petroleum products
2. Compliance with the environmental regulations and laws regarding detrimental pollutants
3. Production of products with an acceptable odor and specification
4. Increasing the performance and stability of motor gasoline
5. Decreasing smoke formation in kerosene
6. Reduction of heteroatom content in fuel oil to a level that improves burning characteristics and is environmentally acceptable

Hydrogenation processes may be classified as destructive and non-destructive. Destructive hydrogenation is a single-stage or multi-stage catalytic process accompanied by the split of carbon-carbon linkages to produce low molecular weight hydrocarbons from high molecular weight fractions. Hydrogenation treatment requires severe process conditions and the use of high hydrogen pressures in order to minimize polymerization and condensation.

Non-destructive hydrogenation is commonly used for the purpose of improving product quality without considerable conversion of the boiling range. Moderate process conditions are applied so that only the more unstable materials are invaded. As a result, nitrogen, sulfur, and oxygen contaminants are exposed to hydrogenolysis to recover ammonia, hydrogen sulfide, and water, respectively.

11.1 Hydrodesulphurization

Growing dependence on heavy oils and residua has arisen, hence of sustainable decrease of conventional crude oil, due to the depletion of reserves all over the world. As a result, current trend to convert as much as possible feedstock to liquid products is causing an increase in the total sulfur in petroleum products. Hydrodesulphurization (HDS), one type of hydrotreating, is currently playing a major role in product improvement when it comes to sulfur problem, moreover it is the most widely used desulphurization technology.

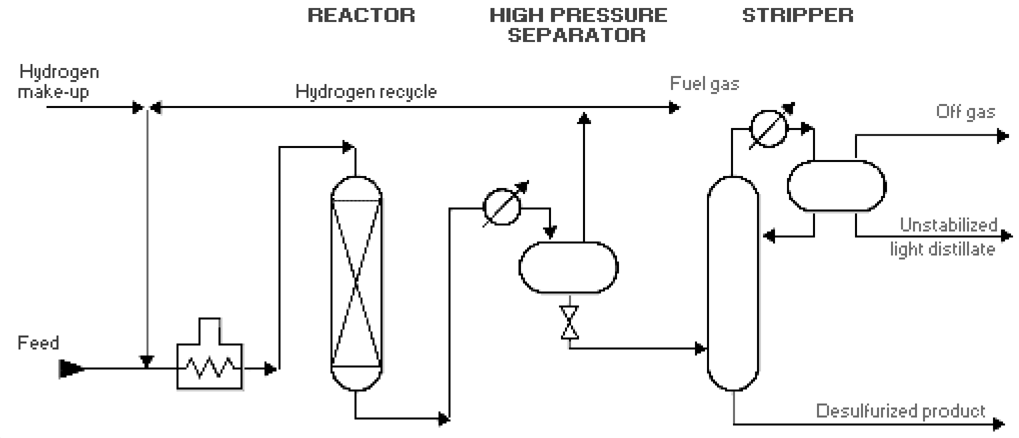


__Figure 23__ Schematic of distillate hydrodesulphurization (SET Labs, 2008)

HDS is a catalytic chemical process commonly used to remove sulfur from natural gas and from refined petroleum products such as gasoline or petrol, jet fuel, kerosene, diesel fuel, and fuel oils. The mechanism is based on reactive adsorption in which metal based adsorbents, such as $CoMo/Al_2O_3$ and $NiMo/Al_2O_3$, capture sulfur to form metal sulfides. The exhausted metal sulfide is sent to regeneration reactor and after reduction with hydrogen is again introduced into the system to remove sulfur from crude. The principal process scheme can be seen in Figure 23, and simplified flow scheme of an oil refinery with possible locations of desulphurization units is shown in Figure 24.

In an industrial hydrodesulphurization unit the hydrodesulphurization reaction takes place in a reactor unit at elevated temperatures ranging from 290 to 445 °C and elevated pressures ranging from 35 to 170 atmospheres of absolute pressure, typically in the presence of a catalyst consisting of an alumina base impregnated with cobalt and molybdenum (usually called a CoMo catalyst) (Speight, 2011). The other important process parameters, such as hydrogen recycle rate, catalyst life, the percentage of sulfur and nitrogen removal for different feedstocks are shown in Table 12.

Table 12 *Process parameters for hydrodesulphurization (Speight, 2011)*

Parameter	Naphtha	Residuum
Temperature (˚C)	300 to 400	340 to 425
Pressure (atm.)	35 to 70	55 to 170
LSHV	4.0 to 10.0	0.2 to 1.0
H_2 recycle rate (scf/bbl)	400 to 1000	3000 to 5000
Catalyst life (years)	3.0 to 10.0	0.5 to 1.0
Sulfur removal (%)	99.9	85.0
Nitrogen removal (%)	99.5	40.0

There are different recently developed technologies. For instance, ConocoPhillips created the first commercial process based on reactive adsorption utilizing nickel on zinc oxide as an adsorbent. This technology is called S-zorb and used for producing ultra-low sulfur fuel. Another research is done by Research Triangle Institute. The development is based on reactive adsorption of sulfur over Fe or Cu promoted alumina-zinc oxide. The main difference of this technology which is called TreND from S-zorb is that it does not require hydrogen nor needs just a little hydrogen (Tuli & Kumar, 2008).

11.2 Process parameters

(i) Hydrogen partial pressure

The high extent of desulphurization can be achieved with the increase of the total pressure in the system. Hence, cocking reactions will be minimized and premature aging of the remaining portion of the catalyst will not be encountered. Hydrotreating processes are carried out at a relatively high pressure of 2 – 5 MPa. Near the upper limit of the set pressure the extent of desulphurization in connection with increasing pressure is negligible.

It was determined that the depth of desulphurization depends on hydrogen partial pressure, because the increase of total system pressure does not substantially contribute to hydrogenation processes. If the hydrogen partial pressure is too low for the selected system, the effectiveness and the service life of catalysts will be decreased. With increasing hydrogen partial pressure up to 3 MPa degree of hydrogenation of sulfur compounds increases very rapidly, and above 30 MPa very slightly (TehnoInfa, 2009).

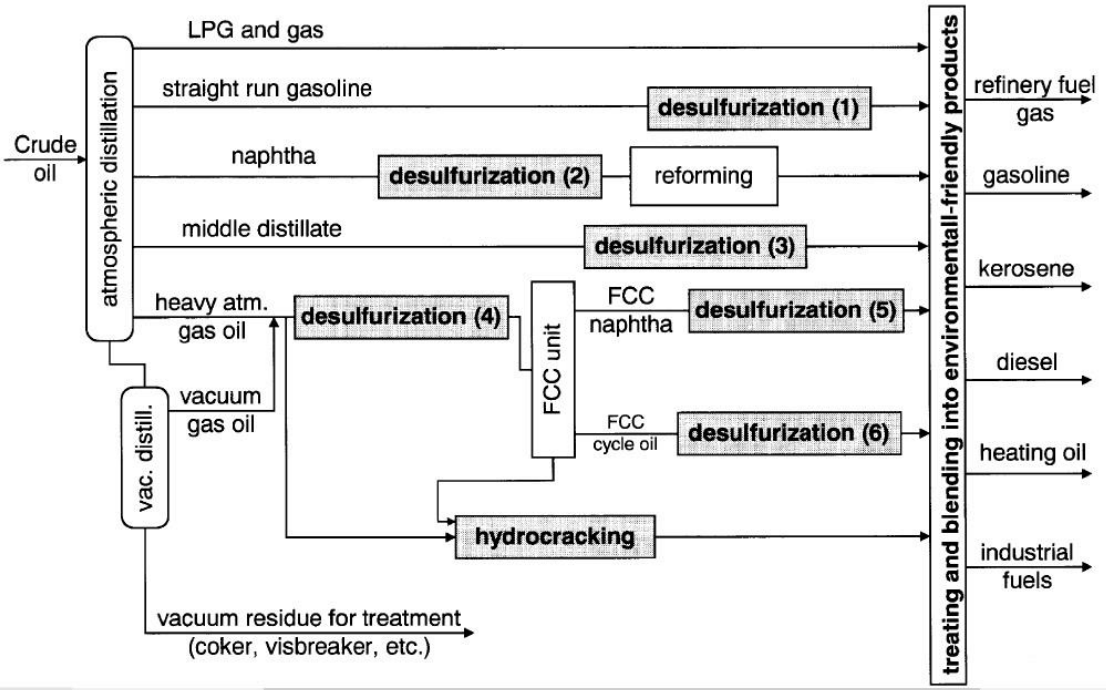


Figure 24 *Simplified flow scheme of an oil refinery with possible locations of desulphurization units (Babich & Moulijn, 2003)*

(ii) Space velocity

As the space velocity is increased, the residence time of feedstock in reactor is decreased, and vice-versa, with the decreasing space velocity the feed contact time with catalyst is increased, hence, the degree of treatment is maximized. However, the low space velocity reduces the amount of feed through the reactor causing reduced plant capacity.

Therefore, there is a maximum allowable space velocity for each feedstock, and a hydrotreatment process is precisely set to this rate.

When selecting the space velocity not only fractional and chemical content of the feed has to be taken into account, but also the state of the catalyst, as well as other process parameters (temperature, pressure) affect the rate of desulphurization (TehnoInfa, 2009).

(iii) Reaction temperature

The optimum reaction temperature depends on the feedstock quality, process conditions and the catalyst activity, and it is in the range of 340 – 400 ˚C. The rate of hydrodesulphurization increases with increasing temperature, reaching a maximum at about 420˚C.

At higher temperatures the rate of hydrogenation is reduced: for sulfur compounds - slightly, and for unsaturated and aromatic hydrocarbons - quite sharply. Consequently, this results in excessive coking reactions and premature catalyst aging rates. For that reason, units are designed to avoid the use of such temperatures (Speight, The Chemistry and Technology of Petroleum, 2007).

(iv) Catalyst life

The loss of catalytic activity is caused by several factors. In normal process conditions, the catalyst deactivation occurs gradually and continuously throughout the cycle due to coke formation, but there are a few points that explain the high rate of deactivation.

Coking occurs due to the presence in the feedstock of high-molecular compounds or by condensation of polynuclear aromatic compounds. In normal operation conditions, a high hydrogen partial pressure and a hydrogenation rate of the catalyst impede the process of coking caused by condensation reactions.

Organometallic compounds decompose and are held on the catalyst surface. Alkali metals can accumulate on the catalyst due to insufficient demineralization of feedstock or because of its contact with the salty water and additives. These metals are unregulated poisons to the catalyst.

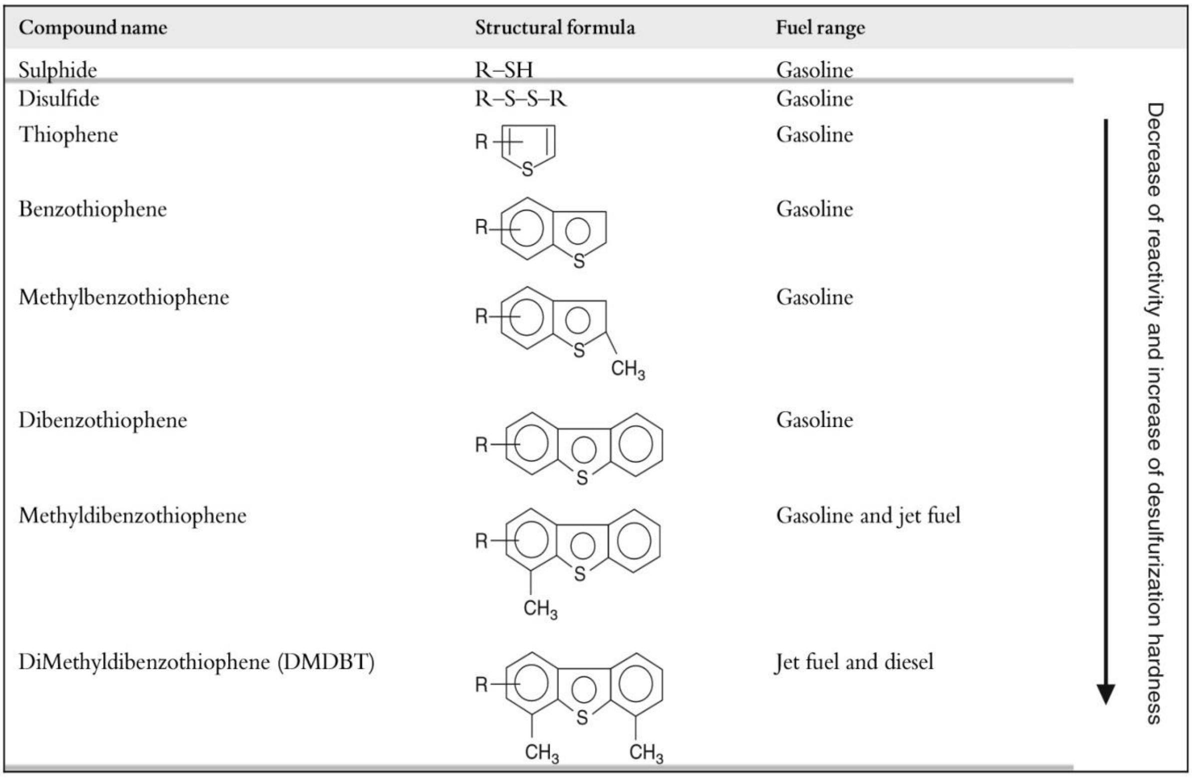
Organic nitrogen compounds present in feedstock are converted into ammonia in hydrogenation processes. Since ammonia is a compound with basic properties, it competes with the reactants at the acid sites of the catalyst and inhibits its activity. Most of the ammonia is removed from the reactor unit with water and, therefore, its effect on catalyst deactivation is low.

Over time, the catalyst activity decreases due to the deposition of catalyst poisons and coke on its surface. Reducing the hydrogen partial pressure in the circulating gas and the exaggeration of the process conditions contribute to coking of the catalyst.

Gradually the catalyst "ages" through recrystallization and change of the surface structure and also due to adsorption on the surface of metals and other substances that blocks the active sites. In this case, the catalytic activity significantly decreases and the catalyst is changed to the new one.

12. Unconventional desulphurization technologies

HDS operates in considerably high temperatures and pressures with hydrogen to regenerate organosulfur compounds into lighter hydrocarbons and hydrosulfides. HDS removes light organosulfur compounds, as mercaptans and thiophenes; however, when it comes to heavier sulfur mixtures like dibenzothiophene and its derivatives it is not as effective. HDS is also an expensive process, for instance, the cost of desulphurization of 20,000 barrel of oil per day is as much as $40 million. Moreover, additional hydrogen and sulfur plant capacities would double the investment into refinery plant (Johnson S. W., 1995).



Compound name	Structural formula	Fuel range
Sulphide	R–SH	Gasoline
Disulfide	R–S–S–R	Gasoline
Thiophene		Gasoline
Benzothiophene		Gasoline
Methylbenzothiophene		Gasoline
Dibenzothiophene		Gasoline
Methyldibenzothiophene		Gasoline and jet fuel
DiMethyldibenzothiophene (DMDBT)		Jet fuel and diesel

Figure 25 *Reactivity of various organic sulfur compounds in HDS versus their ring sizes and positions of alkyl substitutions on the ring (Fahim et al., 2010)*

12.1 Oxidative desulphurization

Oxidative desulphurization (ODS) is an innovative technology that can be used to reduce the cost of producing ultra-low sulfur diesel (Gatan et al., 2004). It has been in focus since 1960's. Different companies like BP, Texaco, Shell were developing suitable ODS technologies to obtain gas oil fractions with low sulfur content. Nevertheless, with more than 80 patents granted and implied several pilot scales, no commercial plant has yet been built (Tuli & Kumar, 2008).

The basic mechanism of ODS is, first the organosulfur compounds present in middle distillate fractions are oxidized to the corresponding sulfoxides and sulfones by an oxidant (such as H_2O_2, ozone, t-butyl hydroperoxide, t-butyl hypochlorite, etc.) and then these sulfoxides and sulfones are removed from diesel by extraction, adsorption, distillation or decomposition .

ODS has more advantages comparing with hydrodesulphurization. The capital expenditure for ODS is less than for HDS as different fractions can be oxidized under low temperature and pressure conditions and expensive hydrogen is not required. It is relevant for small and medium scale refineries for the locations which are far from water pipelines as the use of hydrogen is avoided (Zongxuan et al., 2011).

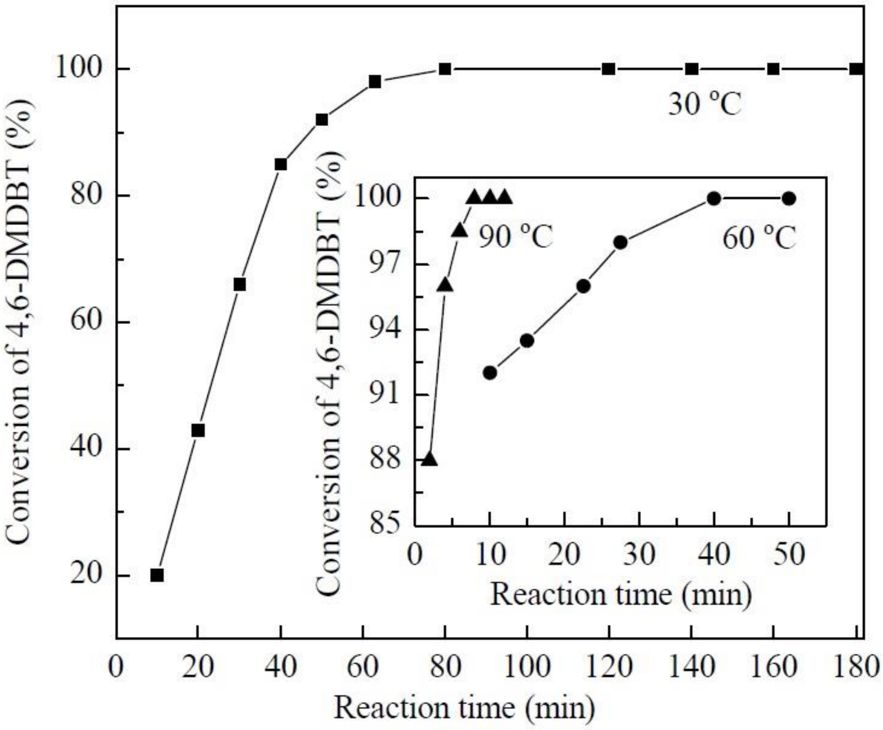


Figure 26 Conversion of 4,6-DMDBT after oxidation with H_2O_2 as a function of reaction time at different reaction temperatures under mild conditions (Zongxuan et al., 2011)

12.2 Biocatalytic desulphurization

The increasing global levels of sulfur content in crude oil have motivated the development of alternate desulphurization technologies. Microbial desulphurization or biodesulphurization (BDS) has gained interest due to the ability of certain biocatalysts to desulfurize compounds (benzothiophene, dibenzothiophene and its derivatives) that are recalcitrant to the currently employed hydrodesulphurization technology.

BDS is a relatively new technological process used to remove sulfur compounds from the crude oil. Special protein-based biocatalysts are needed for BDS. The general idea of BDS is to bring air, whole cell, oil and water into intimate contact, and to produce desulfurized oil stream free of water and biocatalyst cell in a continuously fed, well stirred reactor (Johnson, 1995).

Complex organosulfur compounds, such as dibenzothiophene (DBT) and alkyl DBT, go through different pathway in order to be transformed into more reactive compounds. This pathway is called a sulfur specific desulphurization pathway or simply 4S route. The microorganisms involved in this process are rhodococcus, bacillus, corynobacterium and anthrobacter. The reaction scheme of 4S route is shown in Figure 29 and involves four continuous reaction steps: (i) DBT is oxidized to DBTO (DBT sulfoxides), (ii) DBTO is transformed to DBT sulfones ($DBTO_2$) and (iii) to sulfonate (HPBS), (iv) hydrolytic cleavage to 2-hydroxybiphenyl (2-HBP) and following releases of sulfite or sulfate.

The strong side of BDS is that technology requires less energy and hydrogen. The process is held under ambient temperature and pressure with high selectivity, resulting in decreased energy costs, low emission, and no generation of undesirable side products (Mohebali, 2008).

A conceptual process flow diagram of the BDS process is illustrated in Figure 27. Critical aspects of the process include reactor design, product recovery and oil–water separations. Important new concepts include the use of multiple-staged airlift reactors to overcome poor reaction kinetics at low sulfur concentrations and reduce mixing costs, and the concept of continuous growth and regeneration of the biocatalyst in the reaction system, rather than in separate, external tanks (Monticello, 2000).

12.2.1 Process aspects

Several parameters are substantial in development of BDS process, and the biocatalyst activity is the main one. Other parameters include oil/water ratio, composition of aqueous phase used for biocatalyst suspension during sulfur removal, biocatalyst loading, oil water separation, biocatalyst recycle, recycle of aqueous phase to reduce fresh water usage, and secondary oil separation and purification operations.

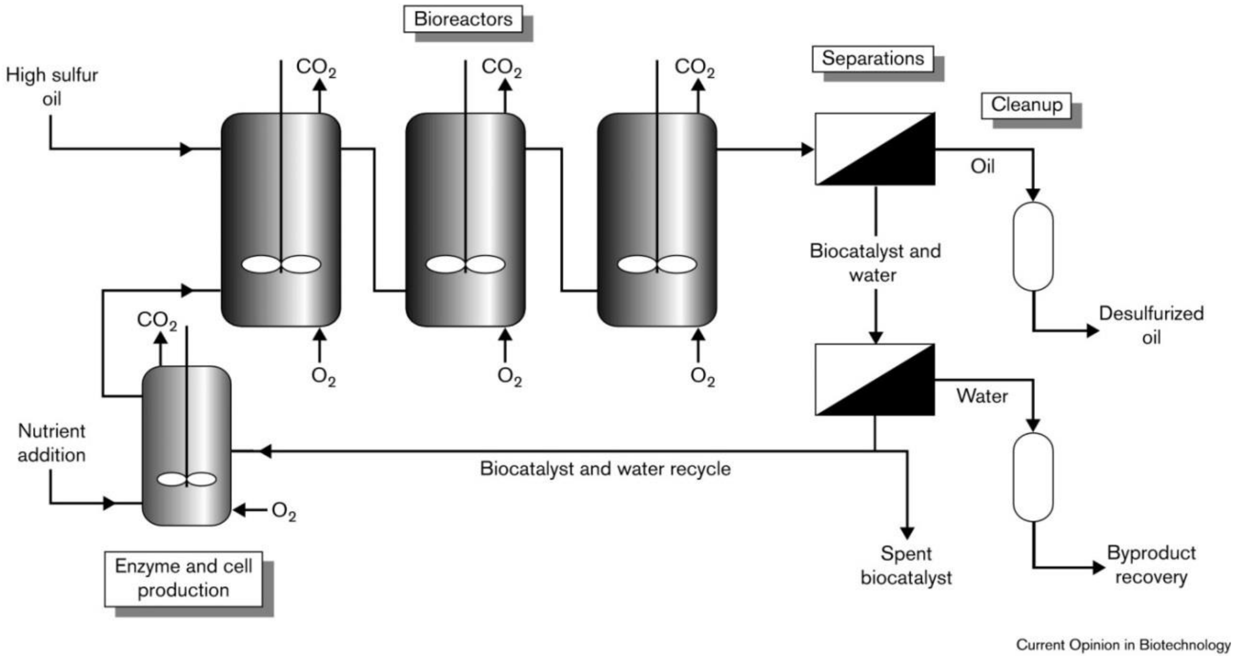


Figure 27 *Conceptual flow diagram for the BDS process (Monticello, 2000)*

A common BDS technology is held in the following steps (Ramirez-Corredores & Borole, 2007):

- Vegetation of the biocatalyst in a fermentative process using appropriate carbon and sulfur sources and other nutrients
- Separation of the biomass from the culture medium
- Use of the biomass as a catalyst for the desulphurization reaction, usually carried out in a completely stirred reactor and in the presence of large quantities of water (at least 1/3 water/oil (W/O) volumetric ratio)
- Separation of the aqueous, oil, and biocatalyst (solid/biomass paste) phases
- Recycling of the biomass paste, to the desulphurization reactor after regeneration /addition of fresh biocatalyst

- Secondary recovery of biocatalyst from the aqueous phase (via filtration, etc.)
- Removal of sulfate via precipitation by lime addition or using other salts
- Removal of the residual water from the desulfurized oil phase (e.g., using high-efficiency separators such as electrostatic separators)

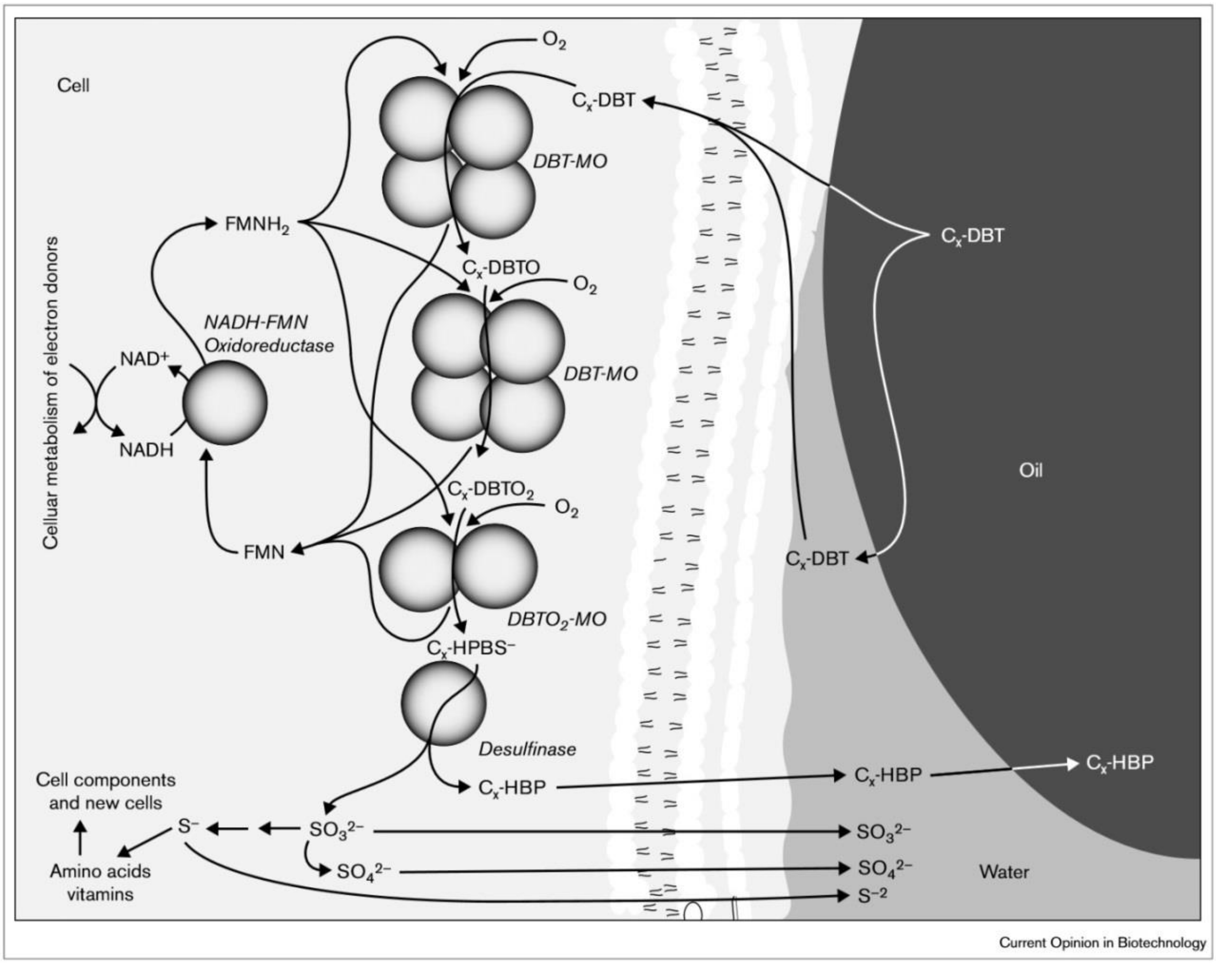


Figure 28 *Conceptual diagram of some of the steps in the desulphurization of oil (Monticello, 2000)*

12.2.2 Barriers for commercialization

Biodesulphurization capital costs are approximately 40-50$ million, which is about half that for hydrodesulphurization. Also operating costs are 15% less. Even though, BDS has certain barriers to use this technology in an industrial scale (Tuli & Kumar, 2008).

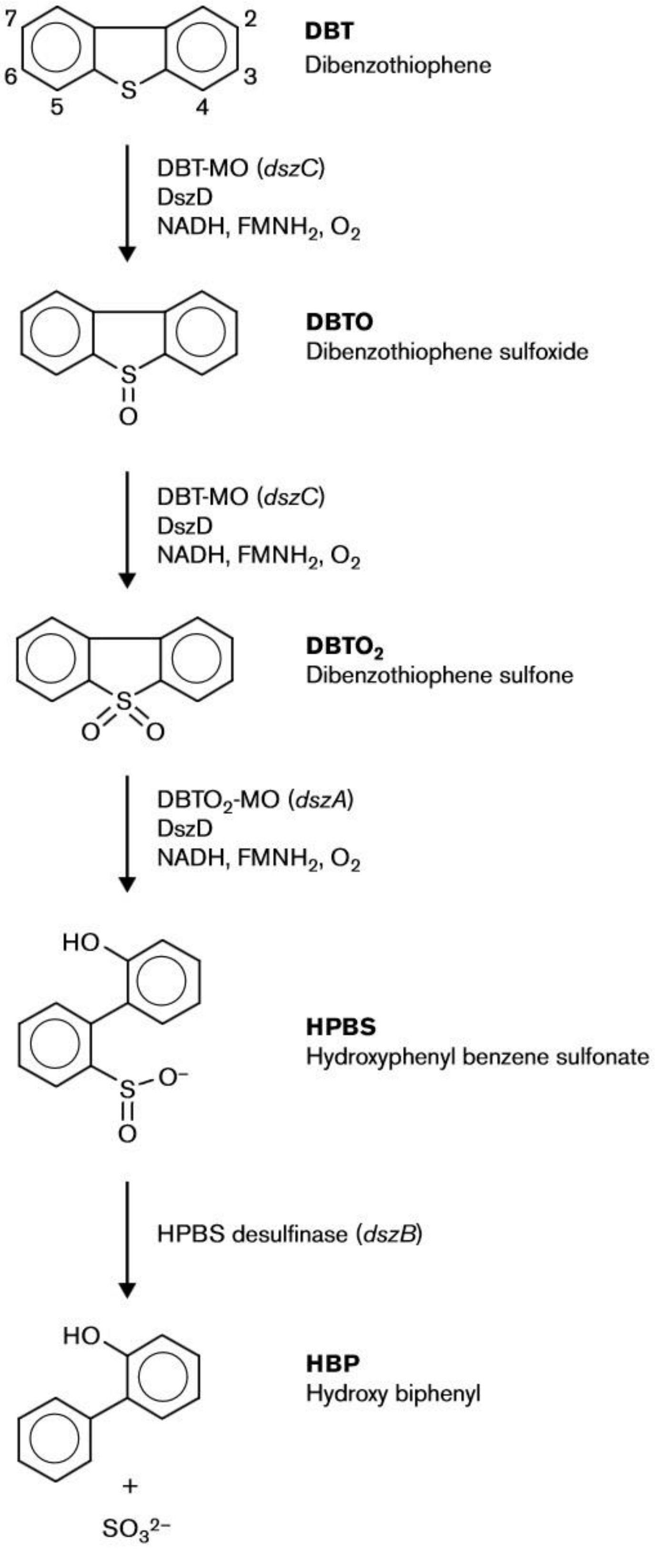


Figure 29 *The "4S" pathway for the biological desulphurization of dibenzothiophene and its derivatives (Monticello, 2000)*

(i) Biocatalyst longevity improvement

First barrier for commercialization of BDS is the biocatalyst longevity. This problem is related to the logistics of sanitary handling, shipment, storage and use of living bacterial strains within the production site and refinery units. The original BDS technology had the acceptable catalyst longevity around 1-2 days. Contemporary design includes production and regeneration units within the BDS process, with the longevity in the range of 200-400 hours (McFarland, 1999). However, highly active and stable biocatalysts adapted to the extreme conditions encountered in petroleum refining have not yet found.

(ii) Poor catalyst selectivity

Poor catalyst selectivity is another problem. Despite the significant progress in improving the technology, organisms that would remove organic sulfur from crude are not selective enough for sulfur compounds and they can remove or destroy the certain amount of hydrocarbons in process. Over the last two decades several research groups have attempted to isolate bacteria capable of efficient desulphurization of oil fractions (Mohebali & Ball, 2008).

(iii) Reactor design

Lack of good reactor design is the next barrier. Several reactor design researches led to advanced process conditions that reduced the influence of mass transport limitations, making the higher volumetric reaction rates possible. Up to date BDS reactors utilize staging, air sparging, and media optimization, hence this reduces the reactor size. However, this also requires downstream processing modifications for emulsion breaking. Moreover, the difficulty of separations increased with increased biocatalyst concentrations due to particle stabilized emulsions (McFarland, 1999).

(iv) Phase contact and separation

Generally bacterial species are responsive to organic solvents. The progress in research of stable and active microorganisms in the presence of non-aqueous solvents is desirable in crude oil fractions upgrading by BDS. In the BDS bioreactor, a limiting factor is the transport rate of the sulfur compounds from the oil phase to the bacterial cell membrane.

Efficiency of sulfur removal is likely to be related to oil droplet size. Therefore, access to organic sulfur by resting cells requires the costly dispersal of the oil fraction in the aqueous phase. The effects of surfactants on bacterial desulphurization of DBT have been investigated in biphasic (oil–water) systems; biodesulphurization has been enhanced by addition of surfactants. It has been suggested that these conditions favored more effective contact between the biocatalyst and the hydrophobic substrate. One problem, which has yet to be resolved, is whether the chemical surfactants would be toxic to the process organisms or act against the characteristic adhesion mechanisms of the bacteria to oil droplet surfaces (Mohebali & Ball, 2008).

(v) Integration to a refinery operations

Integrating a BDS into a refinery is the only way to treat petroleum fractions. Some of the options to integrate BDS units to refinery are given in Figure 30. It is very challenging to make considerable modification of current operations in a refinery. Moreover, BDS processes have to operate at the same speed and reliability as other refinery processes. As a consequence of that employing BDS as a component of refinery operations met with opposition in the petroleum industry (Kilbane & Le Borgne, 2004).

12.3 Novel combined technologies

Convenient desulphurization technologies are not perfect, and considerable work has to be done to improve process parameters and to reduce the energy consumption. Presently available technologies for sulfur removal cannot satisfy the industry requirements and cannot be complied with the market needs. New combined technologies could be one of the solutions to the existing problems.

Nowadays, a lot of novel combined technologies for desulphurization of crude are being reviewed, including the hydrogenation-bacterial catalysis method, the microwave-catalytic hydrogenation method, the three step Biodesulphurization-Oxidative desulphurization-Reactive adsorption (BDS-OD-RA) integrated process, conversion/extraction desulphurization, and the ultrasonic-catalytic oxidation method (Lin et al., 2010).

(i) Microwave-catalytic hydrogenation process for desulphurization

Microwave, catalysis and hydrogenation as an integrated process technology could improve the desulphurization rate and this technology is more efficient as opposed to traditional technology. In this integrated technology HDS catalyst can be regenerated with the help of microwave energy. Moreover, microwave inducement could result in higher sulfur removal effect of chemical desulphurization.

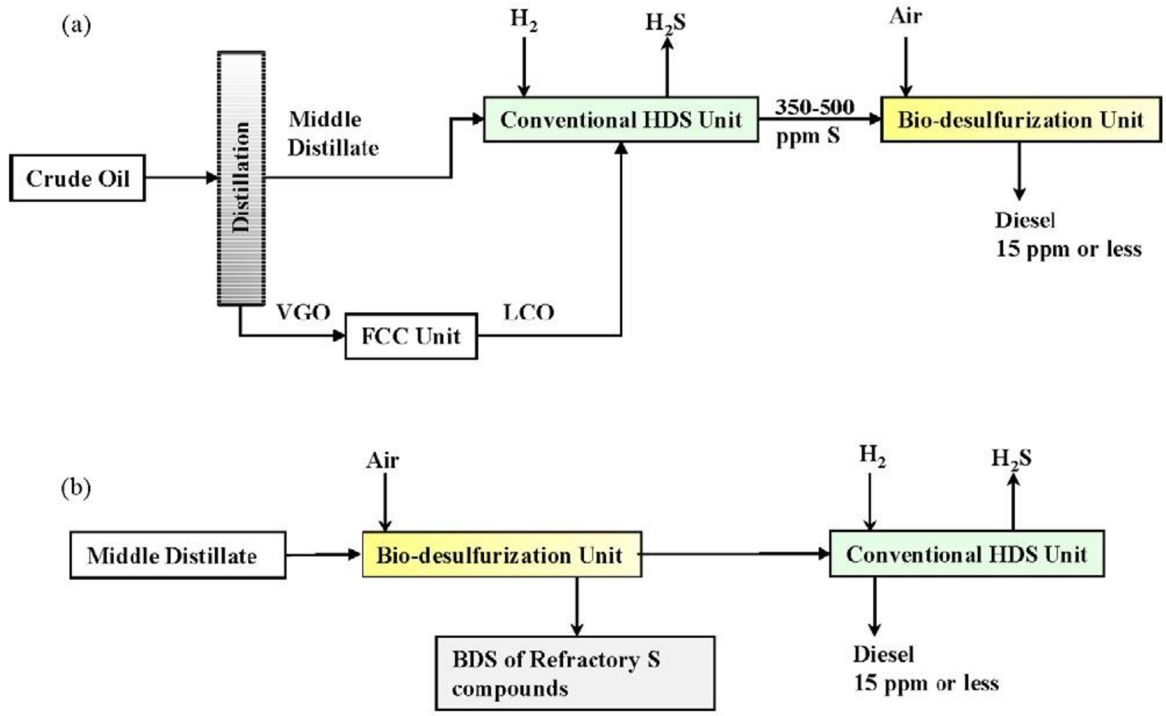


Figure 30 *Options of biodesulphurization in the upgrading of petroleum middle distillates (diesel) to ultra low sulfur levels (a) BDS unit after conventional HDS unit, (b) BDS unit before conventional HDS unit (Stanislaus et al.,2010)*

(ii) BDS-OD-RA three step integrated process

Next promising technology is the integrated BDS-OD-RA process. Generally, the process consists of three step treatment. BDS is the first step where the majority of sulfur compounds are removed, and feed is sent to the second-step treatment where it is oxidized, and finally the remaining sulfur compounds are adsorbed. However, there is a different process conditions for high-sulfur and low-sulfur crude oil in BDS step, anaerobic and aerobic conditions are used respectively.

(iii) Conversion/extraction desulphurization

Conversion/extraction desulphurization (CED) technology was originally introduced by Petro Star Inc. in 1996. It is a combined technology which includes conversion and extraction to remove sulfur compounds from middle distillate products.

The feed is mixed with a stoichiometric amount of oxidant (peroxoacetic acid) at temperatures below 100˚C and at atmospheric pressure. After the oxidation process, the fuel is sent to liquid/liquid extraction unit. It has been reviewed that in laboratory-scale experiments diesel fuel with 4200 ppm sulfur was treated to below 10 ppm sulfur (Babich & Moulijn, 2003).

(iv) Ultrasonic-catalytic oxidation method

Sonocracking$^{\text{TM}}$ technology was developed by SulphCo and applies ultrasound energy to efficiently oxidize sulfur compounds in a water-fuel emulsion containing a hydrogen peroxide catalyst (Babich & Moulijn, 2003). Several successful large-scale ultrasound tests have been carried out in the EU countries and it has been reported to be economically feasible (Lin et al., 2010).

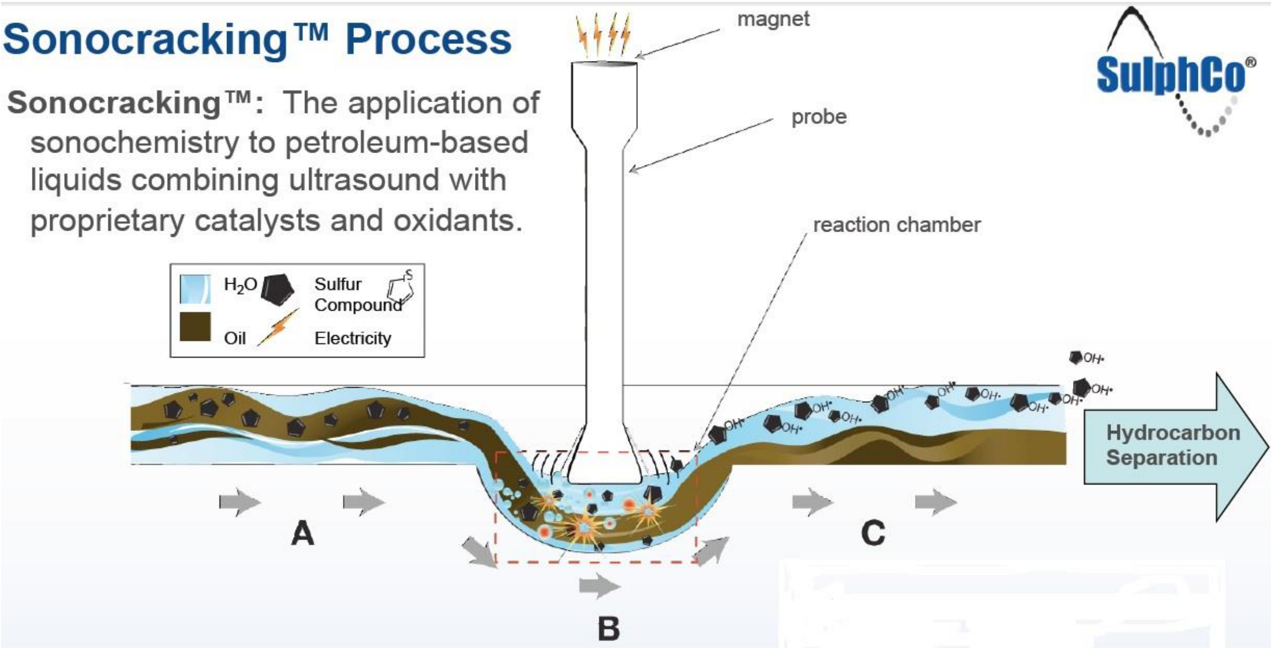


***Figure 31** Effect of ultrasound energy on oxidative desulphurization (SulphCo, 2009)*

The technology operates at 70-80˚C under atmospheric pressure and the residence time for the ultrasound reactor is reported to be only 1 minute (Babich & Moulijn, 2003). Sonocracking^{TM} technology has many advantages, such as simple operation, low cost, low operating conditions, reduced operating cost, and high efficiency.

Graphical illustration of ultrasonic-catalytic oxidation method is given in Figure 31. Feed oil, water, oxidizing agent, and catalyst are mixed in a container and the ultrasonic wave energy is used to convert sulfides into sulfates, sulfoxides, and sulfones, which are then, can be easily removed by separation.

13. Natural gas

13.1 Associated and non-associated gas

Associated gas is a form of natural gas that is associated with the oil in the reservoir. It is also known as associated petroleum gas (APG). The term APG is usually refers to the gas dissolved in the oil; however, theoretically the gas cap is also can be included. When the oil is extracted to the surface, associated gas comes out of solution and usually separated before oil is transmitted via pipeline (PFC Energy, 2007).

Depending on the type of the reservoir, type of lift, how mature is the field, and other factors, volume and chemical content of APG varies from one case to another. When processed and separated from crude oil APG generally exists in combination with other hydrocarbons, such as ethane, propane, butane and pentanes.

Furthermore, raw natural gas contains water vapor, hydrogen sulfide and carbon dioxide, nitrogen and other compounds. Therefore, the natural gas before it is entered into gas pipeline system must be treated. After processing, APG can be utilized in a number of ways, for instance, on-site or regional electricity generation, reinjection for enhanced oil recovery, compression for sale as dry gas, or feedstock for the petrochemical industry (Røland, 2010).

As opposed to associated gas, non-associated gas is in fact never linked to another product. Commonly, industrial projects for the production and refining of this type of gases are absolutely circumscribed by the launch of regional or international markets. In a worst-case scenario, if those export routes are lacking, or because of high transportation expenses, the natural gas reservoirs can remain abandoned for a long time (Rojey et al.,1997).

13.2 Sweet and sour natural gas

Depending on the amount of sulfur compounds present natural gases are classified as sweet dry gas, sour dry gas, sweet wet gas, and sour wet gas. It is presented in Table 13. Figure 32 shows the sour natural gas reserves around the world.

***Table 13** Classification of gases by composition (composition, volume %) (Rojey et al.,1997)*

Category	1	2	3	4
Ethane and higher hydrocarbons	<10	<10	>10	>10
Hydrogen sulfide	<1	>1	<1	>1
Carbon dioxide	<2	>2	<2	>2
Standard designation	Sweet dry gas (non-associated)	Sour dry gas (non-associated)	Sweet wet gas (associated)	Sour wet gas (associated or condensate gas)

13.3 Gas sweetening processes

There is a great number of existing and economically viable gas sweetening processes, and some of them are listed below according to chemical and physical principles used (Arnold & Stewart, 1999):

1. Solid bed absorption:
    - Iron Sponge
    - SulfaTreat® (Licensor: The SulfaTreat Company)
    - Zinc Oxide
    - Molecular Sieves (Licensor: Union Carbide Corporation)
2. Chemical solvents:
    - Monoethanol amine (MEA)
    - Diethanol amine (DEA)
    - Methyldiethanol amine (MDEA)
    - Diglycol amine (DGA)
    - Diisopropanol amine (DIPA)
    - Hot potassium carbonate
    - Proprietary potassium systems
3. Physical solvents:
    - Fluor Flexsorb® (Licensor: Fluor Daniel Corporation)
    - Shell Sulfinol®

- Selexol® (Licensor: Norton Co., Chemical Process Products)
- Rectisol® (Licensor: Lurg, Kohle & Mineraloltechnik GmbH & Linde A.G.)

4. Direct conversion of H_2S to sulfur
   - Claus
   - LOCAT® (Licensor: ARI Technologies)
   - Strertford® (Licensor: Ralph M. Parsons Co.)
   - IFP (Licensor: Institute Francais du Petrole)
   - Sulfa-check® (Licensor: Exxon Chemical Co.)
5. Hydrogen sulfide scavengers
6. Distillation
   - Amine-aldehyde condensates
7. Gas permeation

(i) Solid bed absorption

Solid bed absorption processes are based on the ability of solid particles to remove acid gases through chemical reactions or ionic bonding. The general idea is that the gas stream must flow through a fixed bed of solid particles that separates the acid gases and hold them in the bed. When the solid bed reaches the end of its useful life, the vessel must be removed and replaced (Branan, 2005). Commonly, there are three main processes implemented under this type of sweetening: the iron oxide process, the zinc oxide process, and the molecular sieve process (Arnold & Stewart, 1999).

(i) Chemical solvents

In chemical solvent processes, gas streams containing the acid gases are chemically reacted with a lean solvent in an absorber. The reaction occurs due to the driving force of the partial pressure from the gas to the liquid (Arnold & Stewart, 1999). The solvent absorbs the acid gases and exits the column as a rich solution, which is then sent to a regenerator column where the acid gases are stripped from the solvent (Koch-Glitsch, 2013).

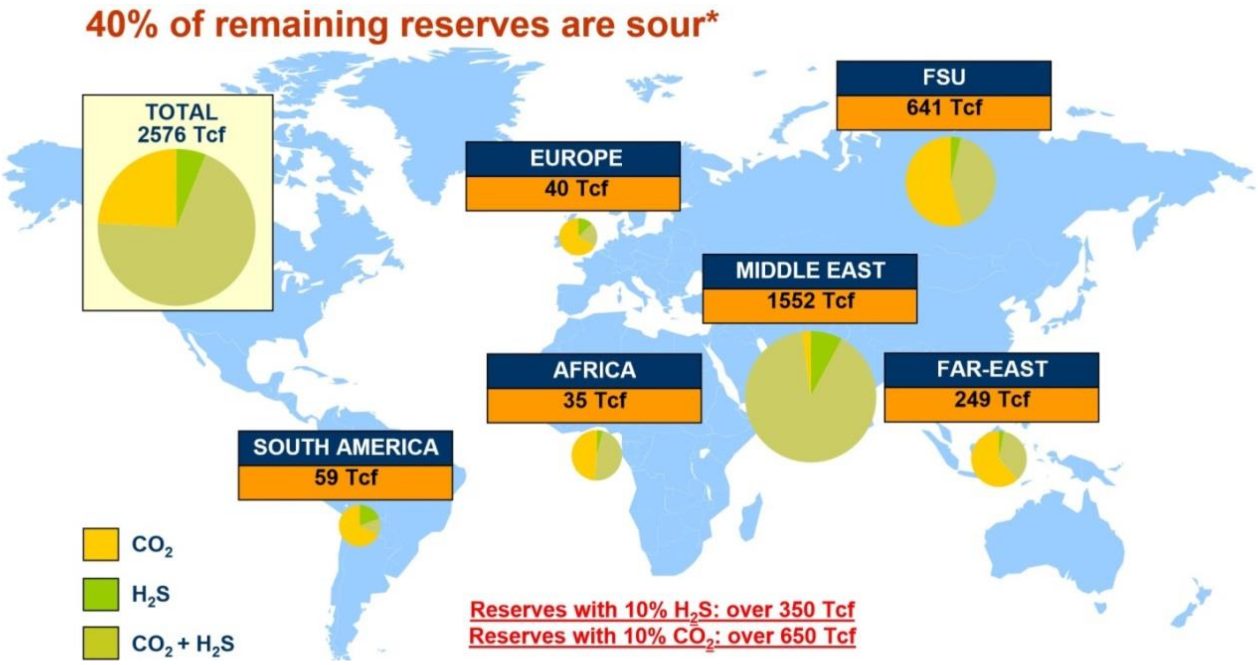


Figure 32 *Sour natural gas reserves around the world (Carrol & Foster, 2008)*

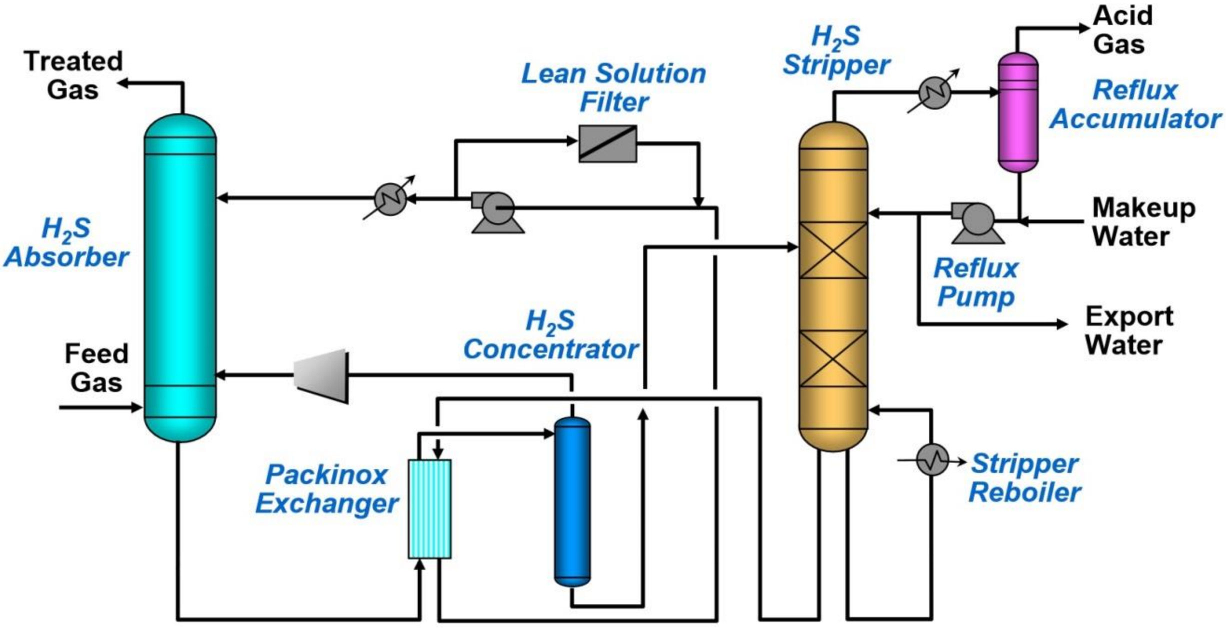


Figure 33 *Selexol® flowscheme for sulfur removal* (UOP, 2009)

(i) Physical solvents

The general idea of physical solvents processes is to use organic solvents to absorb the acid gases. There are no chemical reactions between the acid gas and the solvent, but H_2S and CO_2 is highly soluble within the solvent. Solubility reactions are firstly influenced by partial pressure, and secondarily on temperature. The physical solvent processes are highly effective under higher acid gas partial pressure and lower temperatures (Arnold & Stewart, 1999). There are a number of commercially available technologies within the petroleum industry. The flowscheme of Selexol® process is shown in Figure 33.

Table 14 exhibits the main characteristics of chemical and physical solvents, including advantages and disadvantages of these acid gas removal processes.

Table 14 *Comparison of chemical and physical solvents*

Chemical solvents

Advantages	**Disadvantages**
Relatively insensitive to H_2S and CO_2 partial pressure	High energy requirements for regeneration of solvent
Can reduce H_2S and CO_2 to ppm levels	Generally not selective between H_2S and CO_2
	Amines are in a water solution, and thus the treated gas leaves saturated with water

Physical solvents

Advantages	**Disadvantages**
Low energy requirements for regeneration	May be difficult to meet H_2S specifications
Can be selective to H_2S and CO_2	Very sensitive to acid gas partial pressure

(ii) Direct conversion of H_2S to sulfur

Direct conversion technology is based on chemical reactions to oxidize hydrogen sulfide and to produce elemental sulfur. This technology uses the reactions of H_2S and O_2 or H_2S and SO_2. All reactions involve special catalysts and/or solvents and yield water and elemental sulfur. Several commercially available processes, such as Claus® process, LOCAT® process, Stretford® process (Figure 34), and others have been successfully used to remove H_2S from the gas stream.

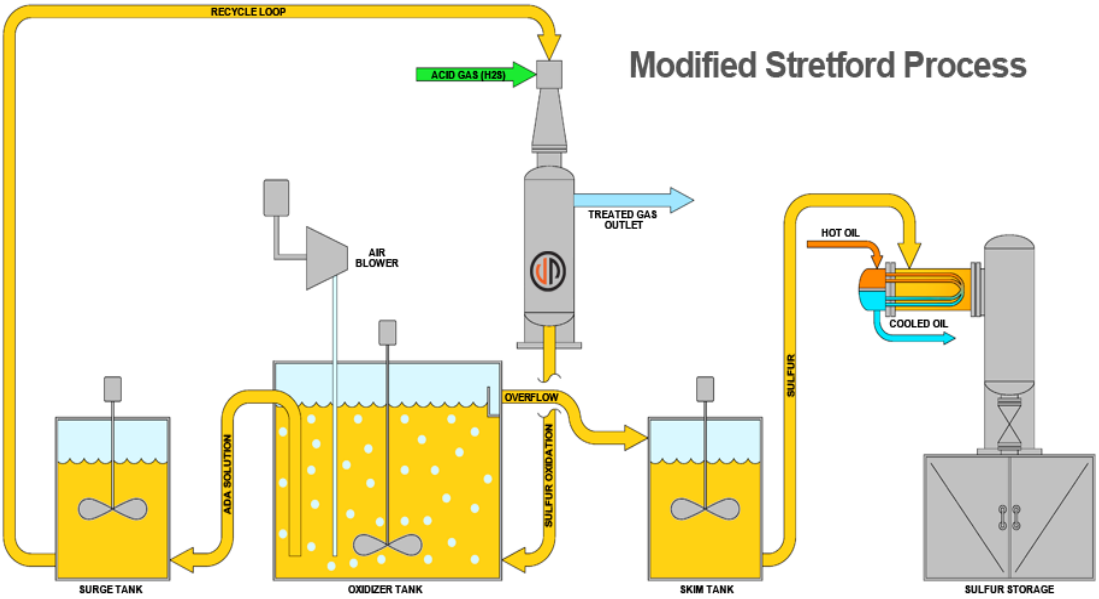


Figure 34 *Modified Stertford® process flow diagram (Joule Processing, 2012)*

It should be noted that direct conversion processes do not release harmful gases like H_2S and CO_2 to the atmosphere, as in the case of previously discussed technologies. The acid gases from chemical and solvent processes can be flared, which would cause of SO_2 release. It is known that allowable level of SO_2 is strictly regulated by environmental authorities, and these limitations are revised periodically (Arnold & Stewart, 1999).

(iii) Hydrogen sulfide scavengers

Sulfide scavengers are based on chemical reactions of commercial additives with one or more sulfide species by converting them into a more inert form. Sulfide scavengers technology is commonly carried out in a continuous sour gas stream. Different scavengers, such as amine-aldehyde condensates, are constantly injected into the system. The most critical parameter is contact time between the scavenger and the sour gas (Arnold & Stewart, 1999).

Effective hydrogen sulfide removal is achieved if there is an irreversible and complete chemical reaction between the scavenger and one or more sulfide species. Upon reaction equilibrium between the three species in solution is achieved, for that reason complete removal of one species serves to remove all three. Insufficient chemical reaction between a species and the scavenger cannot remove all soluble sulfides present (Amosa et al., 2010).

13.4 Process selection factors

Gas sweetening processes were described in the previous chapter. Each of these processes has favored position comparing with others for various cases; hence the following process selection factors should be considered (Kidney & Parrish, 2006):

- The type of acid contaminants present in sour gas stream;
- The concentration of impurities and amount of heavy hydrocarbons and aromatics in the sour gas. For example, COS, CS_2, and mercaptans can affect the design of both gas and liquid treating facilities. Physical solvents tend to dissolve heavier hydrocarbons, and the presence of these heavier compounds in significant quantities tends to favor the selection of a chemical solvent;
- The volume of gas to be treated the temperature and pressure at which the sour gas is available. High partial pressures (3.4 bar or higher) of the acid gases in the feed favor physical solvents, whereas low partial pressures favor the amines;
- The final specifications of the outlet gas;
- The desirability or selectivity required for removing one or more of the contaminants without removing the others;
- The capital, operating, and royalty costs for the process;
- The environmental constraints, including air pollution regulations and disposal of byproducts considered hazardous chemicals.

Moreover, there are different process selection charts (Figures 35-37) which could help to choose the appropriate sweetening processes. In order to do so partial pressure of acid gas in product and in feed has to be known.

14. Refinery of the future

Refinery industry has been developing significantly over the last century. This development is forced by increasing demand for automotive fuels, as well as for gas oils and fuels for domestic central heating, for fuel oil power generation, and for inputs to the petrochemical industries. The following factors have accelerated the development of new processes (Speight, 2011):

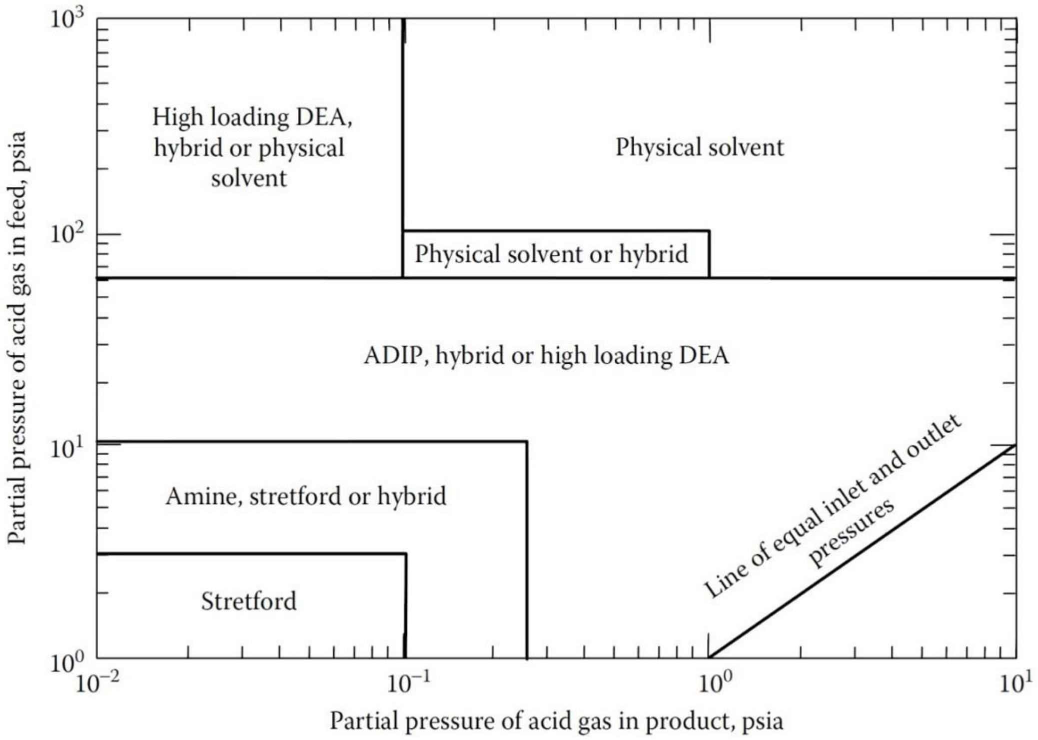


***Figure 35** Process selection chart for H_2S removal with no CO_2 present (Kidney & Parrish, 2006)*

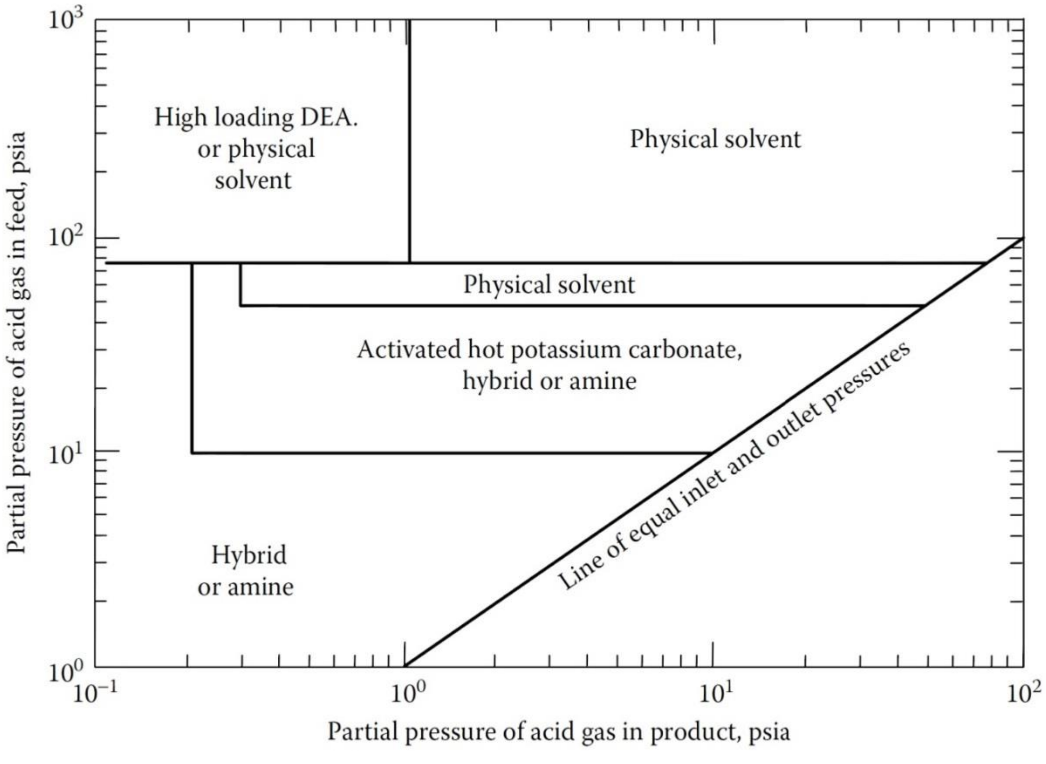


***Figure 36** Process selection chart for simultaneous H_2S and CO_2 removal (Kidney & Parrish, 2006)*

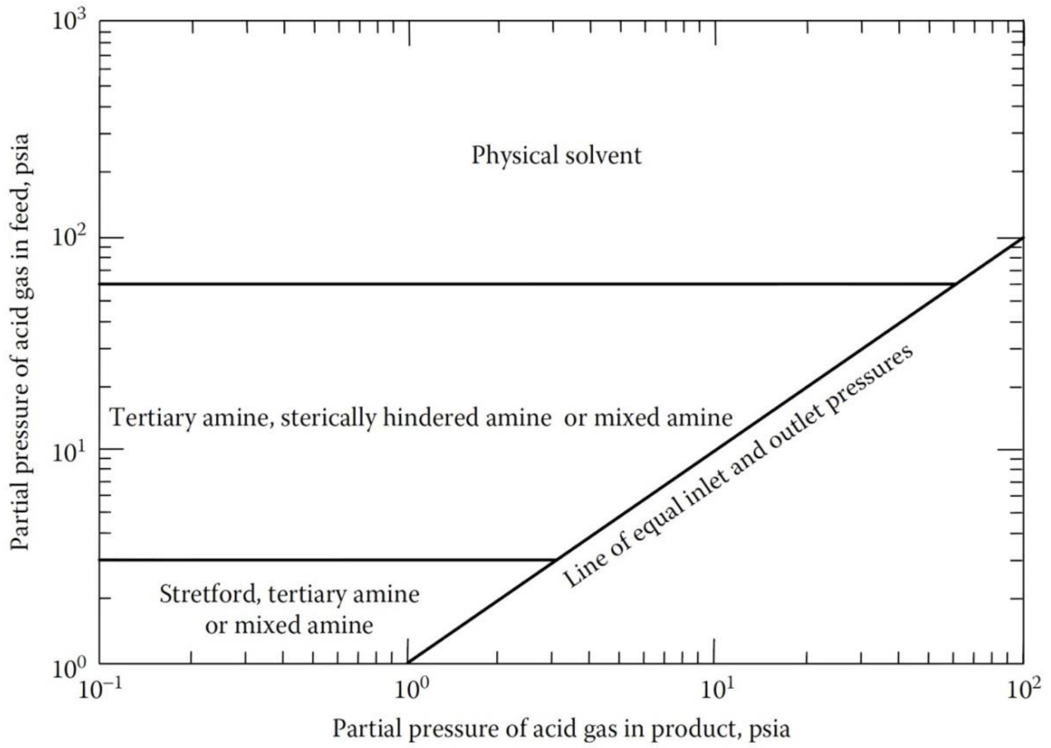


Figure 37 *Process selection chart for selective H_2S removal with CO_2 present (Kidney & Parrish, 2006)*

Table 15 *Natural gas reservoirs with a high H_2S content (Rojey et al., 1997)*

Reservoir	Lithology	Depth (m)	H_2S content (wt %)
Lacq (FRA)	Dolomite and limestone	3100 to 4500	15
Pont d’As-Meillon (FRA)	Dolomite	4300 to 5000	6
Weser-Ems (GER)	Dolomite	3500	10
Asman-Bandar Shipur (IRN)	Limestone	3600 to 4800	26
Urals-Volga (CIS)	Limestone	1500 to 2000	6
Irkutsk (CIS)	Dolomite	2540	42
Alberta (CAN)	Limestone	3506	13
Alberta (CAN)	Limestone	3800	87
South Texas (USA)	Limestone	3354	8
South Texas (USA)	Limestone	5793 to 6098	98
East Texas (USA)	Limestone	3683 to 3757	14
Mississippi (USA)	Limestone	5793 to 6098	78
Wyoming (USA)	Limestone	3049	42

- The high demand for products such as gasoline, diesel, fuel oil, and jet fuel
- Uncertain feedstock supply, caused especially by the changing quality of crude oil, by geopolitical relationships among different nations, and by the emergence of alternate feed supplies such as bitumen from tar sand, natural gas, and coal
- Recent environmental regulations that include more stringent regulations in relation to sulfur in automotive fuels
- Sustainable technological development such as new catalyst and processes

Nowadays, the average quality of crude oil has deteriorated.

To date, according to the statistical information there is a general trend towards reduction of sulfur content of fuels, and this fact will convince that the role of desulphurization increases in importance in the processing operations.

The main developments in desulphurization will follow major paths, such as:

- Advanced hydrotreating (new catalyst, catalytic distillation, processing at mild conditions)
- Reactive adsorption (type of adsorbent implemented, process design)
- Oxidative desulphurization
- Biocatalytic desulphurization
- Combined technologies

Several decades later, the need for hydrogen will be reduced, as new desulphurization technologies and evolution of the older ones are expected to be developed.

In the year 2030 the standard American refinery will be placed at an existing refinery site. That will be mainly due to economic and environmental considerations, as it will be difficult to construct the new refineries at another site. Numerous existing refineries may still be in use, but a lot of processing technologies will be more efficient and more high-tech. Moreover, the main concern for refiners will be the energy efficiency of processing units in order to reduce the cost operating expenses (Speight, 2011).

14.1 Global refinery capacity requirements in the future

Table 16 and Figures 38-40, which are taken from OPEC's annual World Oil Outlook, exhibit information on global crude distillation capacity and desulphurization capacity additions. Improvements in product quality specifications which are previously discussed will influence in considerable desulphurization capacity additions in order to reduce the sulfur level in refined products. It is known that OECD countries are already legislated ultra low sulfur regulations for automotive fuels, further development will be expected in non-OECD countries, because they are also reducing the average sulfur content to low and ultra low levels. It is forecasted that 22 mb/d of additional desulphurization capacity will be required globally by 2035. This number is the largest volume of capacity additions in the period to 2035 (OPEC, 2012).

Table 16 *Global capacity requirements by process (millions of barrels/day) 2011-2035 (OPEC, 2012)*

	Existing projects	Additional requirements		Total additions
	to 2015*	to 2015	2015–2030	to 2035
Crude distillation	**6.0**	**0.7**	**8.2**	**14.9**
Conversion	**4.7**	**1.1**	**5.8**	**11.6**
Coking/Visbreaking	1.5	0.0	0.6	2.1
Catalytic cracking	1.2	0.1	0.5	1.8
Hydro-cracking	2.0	1.0	4.7	7.7
Desulphurization	**6.2**	**3.0**	**12.8**	**22.0**
Vacuum gasoil/Resid	0.2	0.3	1.5	2.1
Distillate	4.5	2.2	8.8	15.5
Gasoline	1.4	0.6	2.4	4.4
Octane units	**1.7**	**1.3**	**2.5**	**5.4**
Catalytic reforming	1.3	1.3	1.4	4.0
Alkylation	0.2	0.0	0.1	0.3
Isomerization	0.2	0.0	1.0	1.1

The most part of desulphurization capacity additions is planned in Asia (10.4 mb/d), the Middle East (3.4 mb/d), Latin America (3.3 mb/d), and the FSU (2.9 mb/d). This is mainly due to expansion of refining base and demand for petroleum products, also tightened nationwide and exported average quality specifications. Figure 40 the data regarding desulphurization capacity additions to the main distillate groups of petroleum products. It can be seen that in the forecasting period from 2011 to 2035, more than 60%

of global desulphurization capacity additions (14 mb/d) are for the desulphurization of middle distillates, whereas 27% for gasoline (6 mb/d), and the rest for vacuum gasoil/residual fuel (2 mb/d).

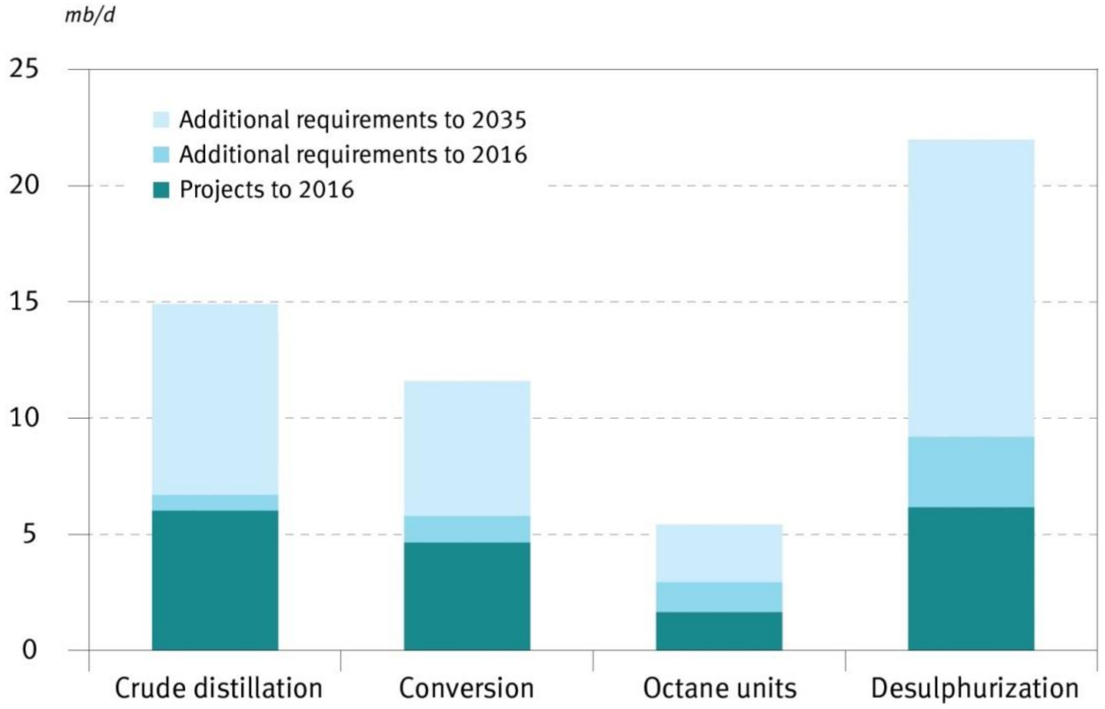


Figure 38 *Global capacity requirements by process type, 2011-2035 (OPEC, 2012)*

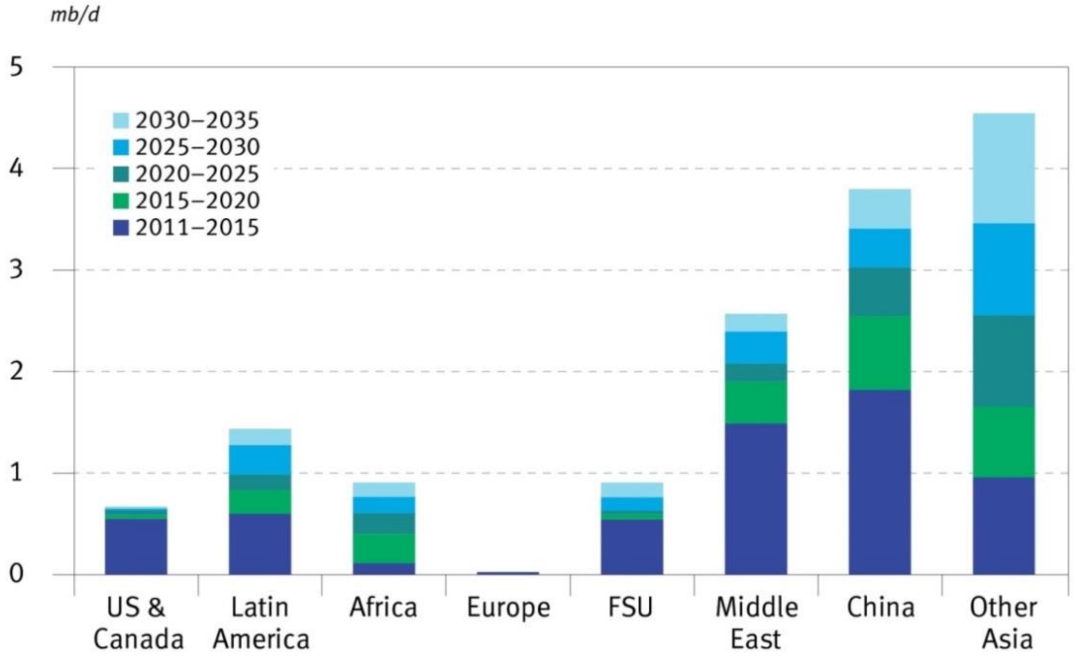


Figure 39 *Crude distillation capacity additions, 2011-2035 (OPEC, 2012)*

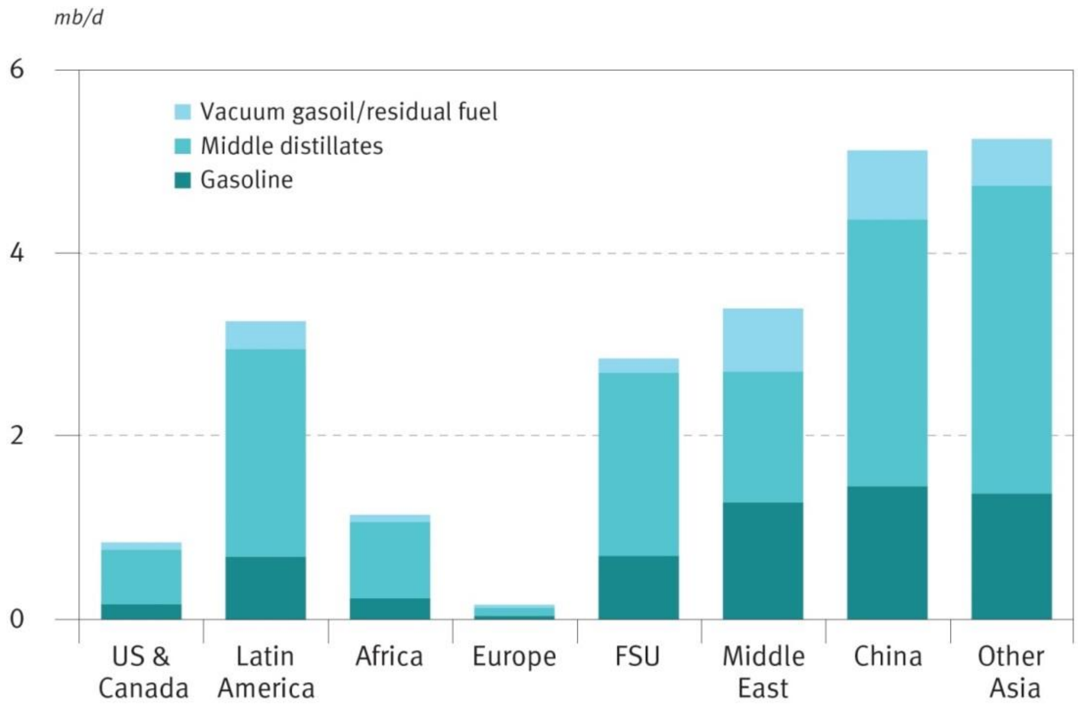


***Figure 40** Desulphurization capacity requirements by product and region, 2011-2035 (OPEC, 2012)*

15. *Effect of organosulfur compounds on natural gas properties*

Natural gases always have water associated with them, as they are saturated with water in the reservoir. When the hydrocarbons are extracted from underground water is also produced straight from the reservoir. Generally, the water contents of sour gases are defined as a molar average of the solubility of water in the hydrocarbons, hydrogen sulfide, and carbon dioxide (Robinson et al.,1977). The accurate prediction of equilibrium water contents of natural gases is extremely important, especially for sour gases.

Distinct knowledge of phase behavior in water – sour gas systems is essential when it comes to design and operation of production and refining facilities, as well as natural gas pipelines, as considerable amount of gases contain acid gases and water. By preventing the formation of condensed water the risk of related problems can be reduced (Mohammadi et al., 2005).

The first problem related with water content of sour gases is corrosion. The lifetime of natural gas pipelines is affected by the rate at which corrosion occurs. The second problem is the formation of hydrates due to the presence of water in natural gas. Hydrates formation leads to safety hazards to production/transportation/injection systems and to considerable economic risks. The last, but not the least problem is two-phase flow in pipelines (Bahadori, 2011).

The risk of the occurrence of the problems mentioned above can be increased if the gas contains even small amount of hydrogen sulfide or carbon dioxide. That is mainly because the solubility of water in H_2S and in CO_2 differs significantly from the solubility of water in hydrocarbon systems as shown on Figure 41 (Carroll, 2002). This fact can possibly be explained by the discrepancy of molecular structures of these compounds. For instance, hydrogen sulfide has higher polarity than hydrocarbon components found in natural gas because of the asymmetric arrangement of its atoms. Water is strongly polar material itself, as a hence, water will have higher solubility in materials with higher polarity (Lukacs & Robinson, 1963).

The mutual solubility of hydrogen sulfide and carbon dioxide differs substantially with system temperature and pressure. Thus, the presence of sour gas, such as H_2S, and the presence of acid gas, such as CO_2, in a natural gas mixture would result in a raise in the water content at any given temperature and pressure (Mohammadi, Samieyan, & Tohidi, 2005).

15.1 Pure components behavior

From the previous chapters it is known that the natural gas is a complex mixture. Each component of the natural gas represents unique characteristics which essentially influences on gas behavior. The graphical presentation of this theory is shown in Figure 41, which demonstrates how the water content of pure components of methane, carbon dioxide, and hydrogen sulfide changes with increasing pressure at 120ºF. It is undoubtedly that all three substances show the diversity of behavior that occurs.

It can be seen that at low pressures the water content does not differ considerably for all three components. Generally, at this low pressure the water content is a function of temperature and pressure. However, with increasing pressure the phase behavior for the three components starts to be different.

The water content of methane, which can be considered as sweet gas, steadily decreases as the pressure increases. When it comes to carbon dioxide, the water content declines until the pressure reaches 1000 psia, after that there is an opposite tendency and the water content increases again. Lastly, hydrogen sulfide liquefies. Because of this unique behavior the water content exhibits discontinuity. It should be noted that at lower temperatures CO_2 behaves similarly and liquefies too.

It is reasonable to assume that the characteristics of three pure components would be matched with the behavior of gas mixtures (Carroll, 2002). Sour gases which contain a little volume of CO_2 and H_2S will have the phase behavior in a similar manner to pure methane. The water content of these gas mixtures will be continually declining as a function of pressure. Acid gas mixtures will behave like pure CO_2, but they will not form a second liquid. Sour mixtures with high content of H_2S will behave almost like pure H_2S. These gases under certain value of pressure and temperature will be in a liquid phase (Carroll, 2002).

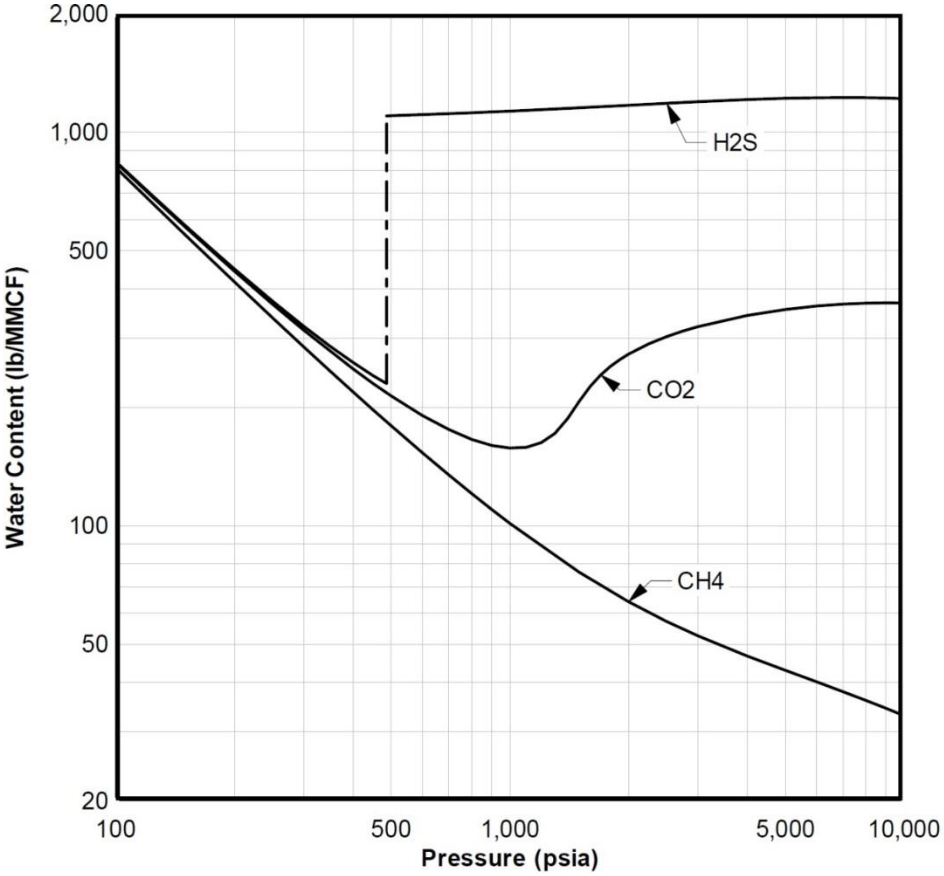


Figure 41 *Water content of three gases at 120℉ (50°C) (Carroll, 2002)*

15.2 Estimation of water content in sour gases

It is believed that sour/acid gases deteriorate the quality of natural gas by affecting the water content of those natural gases. In this subsection the water content of several gases with simplified content and existing gas fields is calculated using the AQUALIBRIUM software, version 3.01. There is a description of this software on the official website of FlowPhase®. There it says that AQUALIBRIUM is a software package for systems containing water, hydrogen sulfide, carbon dioxide, and light hydrocarbons. It has a well-deserved reputation for being amongst the most accurate software for equilibrium calculations in these systems, especially for acid gas + water systems.

First, the water content of natural gases with simplified composition was calculated. Only methane and hydrogen sulfide were taken into consideration to study the general behavior of those gases under three different conditions, reservoir, wellhead, and end-pipe conditions. The values of those parameters are generally accepted in natural gas production operations; moreover, it should be noted that there are other reservoir and surface pressure/temperature conditions.

Figure 42 presents the water content lines versus increasing hydrogen sulfide content of several gases. It is obvious that with increasing content of H_2S the water content also increases significantly. For instance, the gas with high sour content 75% H_2S carries 72% more water vapor as compared to sweeter gas with 15% H_2S.

The result also shows that the water depending on conditions starts to condense out of the gas. Under reservoir conditions the gas holds the largest amount of water, while under end-pipe conditions the water is decreased to a minimum level.

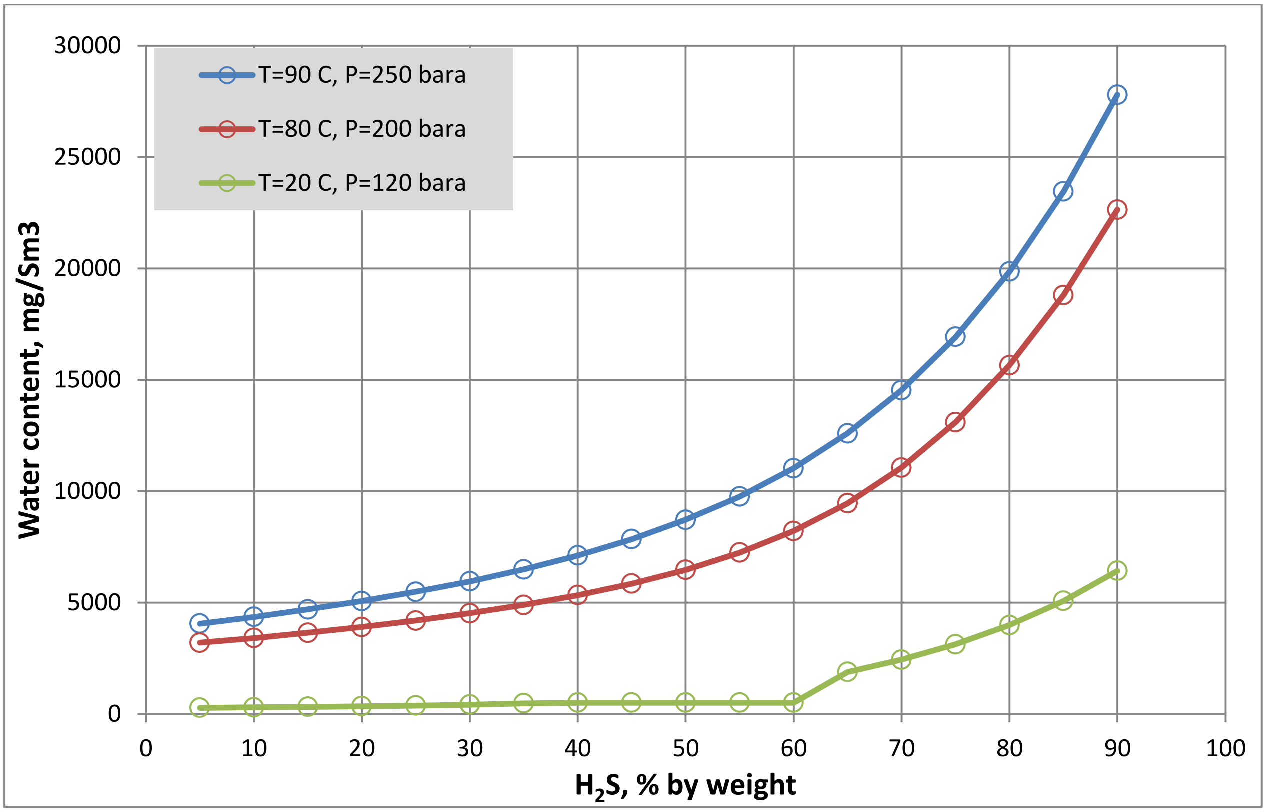


Figure 42 *Water content versus H_2S content of natural gases with simplified composition*

Table 17 *Water content of selected natural gases calculated with AQUALIBRIUM*

Conditions	Pressure, bara	Temperature, ºC	Water content, mg/Sm^3			
			Lacq	Kirkuk	Parentis	Kashagan
Reservoir	250	90	5196	4099	3612	5104
Wellhead	200	80	4004	3224	2867	3954
End pipe	120	20	359	282	240	372

Table 18 Composition of selected natural gases

Component	Lacq (France)	Kirkuk (Iraq)	Parentis (France)	Kashagan (Kazakhstan)
Methane	69.0	56.9	73.6	58.77
Ethane	3.0	21.2	10.2	9.01
Propane	0.9	6.0	7.6	4.54
Butanes	0.5	3.7	5.0	2.29
C_{5+}	0.1	1.6	3.6	1.49
Nitrogen	1.5	-	-	1.01
H2S	15.3	3.5	-	17.81
CO2	9.3	7.1	-	5.08

Table 17 gives the results on water content calculation for the gases from different parts of the world. The composition of the natural gases under studies is given in Table 18. It can be seen that sour gases from Lacq and Kashagan field exhibits undesirable behavior. The high sourness of these gases explains the higher values of water content in comparing with other sweeter gases from Kirkuk and Parentis fields. When it comes to pressure and temperature conditions, there is a common tendency for all four gases. The water vapor starts to condense out of the gas solution, and the water vapor values condensed at the wellhead equal to 1192 mg/Sm^3 and 1150 mg/Sm^3 for Lacq and Kashagan fields respectively, and at the end-pipe the values are 3645 mg/Sm^3 and 3582 mg/Sm^3 which is more or less the same.

It is of vital importance to know the amount of difference between the water content at reservoir conditions and the water condensed at the receiving terminal, as by knowing it the dehydration facilities can be designed and the formation of hydrates can be removed.

Table 19 *Water content of gases with simplified composition calculated by AQUALIBRIUM*

H_2S, weight %	$CH_{1,}$ weight %	Water content, mg/Sm^3	Water content, mg/Sm^3	Water content, mg/Sm^3
90	10	27796	22638	6421
85	15	23446	18802	5073
80	20	19860	15652	3990
75	25	16923	13096	3123
70	30	14533	11057	2431
65	35	12597	9456	1881
60	40	11030	8211	505
55	45	9757	7239	505
50	50	8712	6468	505
45	55	7844	5844	505
40	60	7113	5328	505
35	65	6489	4892	471
30	70	5950	4517	417
25	75	5478	4190	375
20	80	5061	3900	342
15	85	4690	3640	315
10	90	4355	3406	291
5	95	4052	3193	271

Summary

New petroleum product specifications have had profound impact on refineries' business philosophy worldwide. Petroleum companies are investing vast amount of money to introduce breakthrough technologies and to upgrade existing ones.

After in-depth analysis of existing commercial and semi-commercial desulphurization technologies it can be concluded that those technologies cannot satisfy the industry requirements and cannot be complied with the market needs. Conventional hydrodesulphurization is very expensive (desulphurization of 20,000 barrel of oil is as much as $40 million) and energy intensive sulfur removal technique. HDS operates at elevated temperatures (290 to 445˚C) and pressures (35 to 170 atm.), uses very costly hydrogen, removes only easy sulfur (hydrogen sulfide, thiols, etc.), and reduces the quality of refined products. As a hence, decreased energy is returned on energy invested and the impact on the environment is increased. Time and money being spent on research and development for the hydrodesulphurization could be better invested into developing alternative technologies.

It is known that organosulfur removal operations are implemented at surface conditions. But is it the only way to desulfurize hydrocarbon feeds? One of the revolutionary ideas is to develop in-situ or downhole sulfur capture technologies (*DoSCap* technology {Darkhan Duissenov}). Crude oil and natural gas with high sulfur content could be upgraded in the source rock and desulfurized before hydrocarbons are transported to surface. By implementing the *DoSCap* technology additional CAPEX and OPEX would be reduced considerably. The costs of lost time, the replacement of materials of construction, and the constant personnel involvement caused by corrosion, would be avoided. Finally, the commercial value of crude oil would be increased by about 10-15%.

However, the scientists involved in research of the problem under consideration are focused on more immediate challenges and working with currently available techniques and tools. One of the alternatives could be the integration of biodesulphurization process units into existing refineries. There are two options, first option is to put BDS before conventional HDS, and second option is to implement BDS after conventional HDS. In order to do so significant modification of current operations is needed. Biocatalytic desulphurization involves certain type of bacterial strain in order to selectively remove sulfur compounds with high-boiling temperature (thiophenes, dibenzothiophenes, and their alkyl derivatives).

Another alternative is the implementation of combined technologies. In combined technologies the processes could be based on existing sulfur removal techniques, such as oxidative desulphurization, biocatalytic desulphurization, and hydrogenation processes. Furthermore, base technologies could be complemented by various physical forces and chemical reactions. Microwave energy, catalysis and hydrotreatment together can improve the effect of desulphurization and some results were already gained. Also the combination of ultrasonic/microwave and electrostatic fields with oxidative desulphurization will lead to improved process parameters and higher desulphurization rates (Lin et al., 2010).

What is clear for now is that the alternative technologies mentioned above certainly have barriers for commercialization, and most of them have been met with certain opposition within the petroleum industry. The situation threatens to become more challenging with increasing sulfur content trend. While novel technologies are being developed to remove the organosulfur compounds, there is little doubt that utilization of the sour resources will have a negative impact.

Conclusion

- The authorities and environmental agencies are trending down the level of sulfur in petroleum products worldwide. The main purpose of those regulations is to yield high quality fuels with sulfur content less than 10 ppm. It is expected that by 2025 the maximum allowable level of sulfur for gasoline(10 ppm in US & EU, 20 ppm in FSU, 25 ppm in the Middle East) and for diesel (10 ppm in US & EU, 15 ppm in FSU, 40 ppm in Latin America) will be reduced tremendously.
- Conventional HDS is a very, very expensive process which uses elevated pressures and elevated temperatures; moreover HDS is not highly efficient and consumes outrageous amount of energy, resulting in decreased energy returned on energy invested and the increased impact on the environment;
- Biocatalytic biodesulphurization is an effective tool in removal of heavy sulfur compounds as dibenzothiophenes and their alkyl derivatives. Biocatalyst converts dibenzothiophene into 2-hydroxybiphenyl and sulfate via 4S pathway without any change of fuel heating value.
- New integrated technologies such as BDS-OD-RA (desulphurization rate 85-95% for crude oil in anaerobic conditions, 94-95% in aerobic conditions), combined hydrogenation-biodesulphurization technologies (bacterial strains *Rhodococcus erythropolis*, *Arthrobacter paraffineus*, *Bacillus sphaericus*, *Rhodococcus rhodochrous*), desulphurization processes involving ultrasonic-catalytic oxidation (simple operation, low cost, low temperature, high efficiency) could be an excellent alternatives to conventional desulphurization technologies.
- Distinct knowledge of phase behavior in water – sour gas systems is essential when it comes to design and operation of production and refining facilities, as well as natural gas pipelines, as considerable amount of gases contain sour gases and water. By preventing the formation of condensed water the risk of related problems can be reduced.

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Appendices

Table 20 *Estimated proved reserves holders as of January 2013 (Rachovich, 2012)*

Rank	Country	Proved reserves (billion barrels)	Share of total
1.	Venezuela	297.6	18.2%
2.	Saudi Arabia	265.4	16.2%
3.	Canada	173.1	10.6%
4.	Iran	154.6	9.4%
5.	Iraq	141.4	8.6%
6.	Kuwait	101.5	6.2%
7.	UAE	97.8	6.0%
8.	Russia	80.0	5.0%
9.	Libya	48.0	2.9%
10.	Nigeria	37.2	2.3%
11.	Kazakhstan	30.0	1.8%
12.	China	25.6	1.6%
13.	Qatar	25.4	1.6%
14.	United States	20.7	1.3%
15.	Brazil	13.2	0.8%
16.	Algeria	12.2	0.7%
17.	Angola	10.5	0.6%
18.	Mexico	10.3	0.6%
19.	Ecuador	8.2	0.5%
20.	Azerbaijan	7.0	0.4%
21.	Oman	5.5	0.3%
22.	India	5.48	0.3%
23.	Norway	5.37	0.3%
World total		1,637.9	100
Total OPEC		1,204.7	73.6

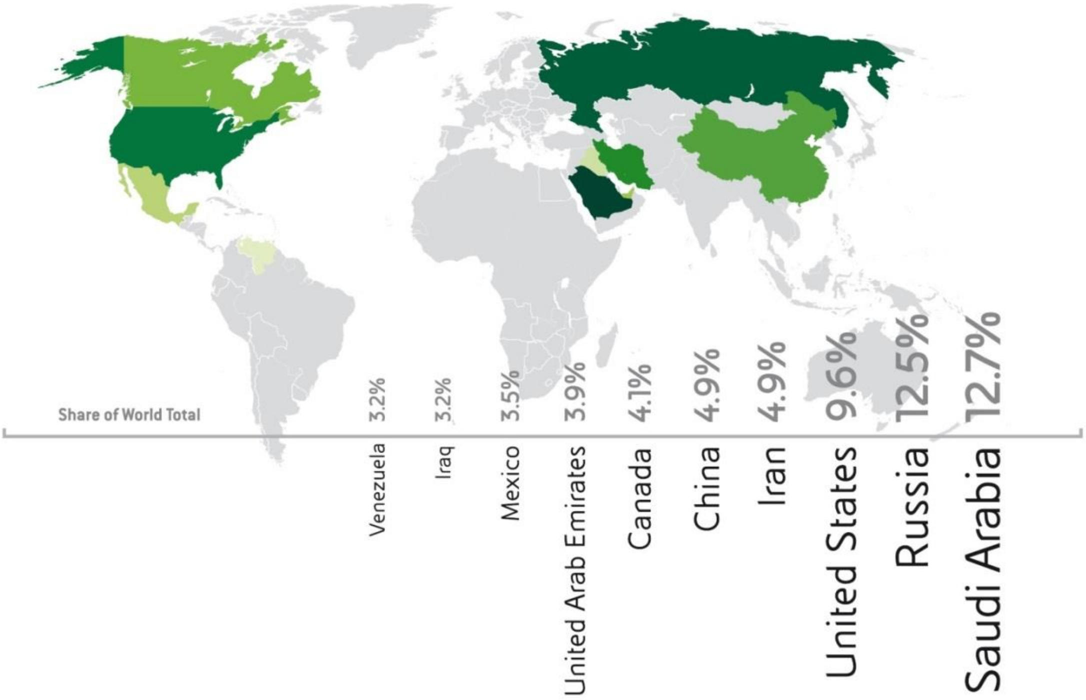


Figure 43 *The world top 10 oil producers (Eni, 2012)*

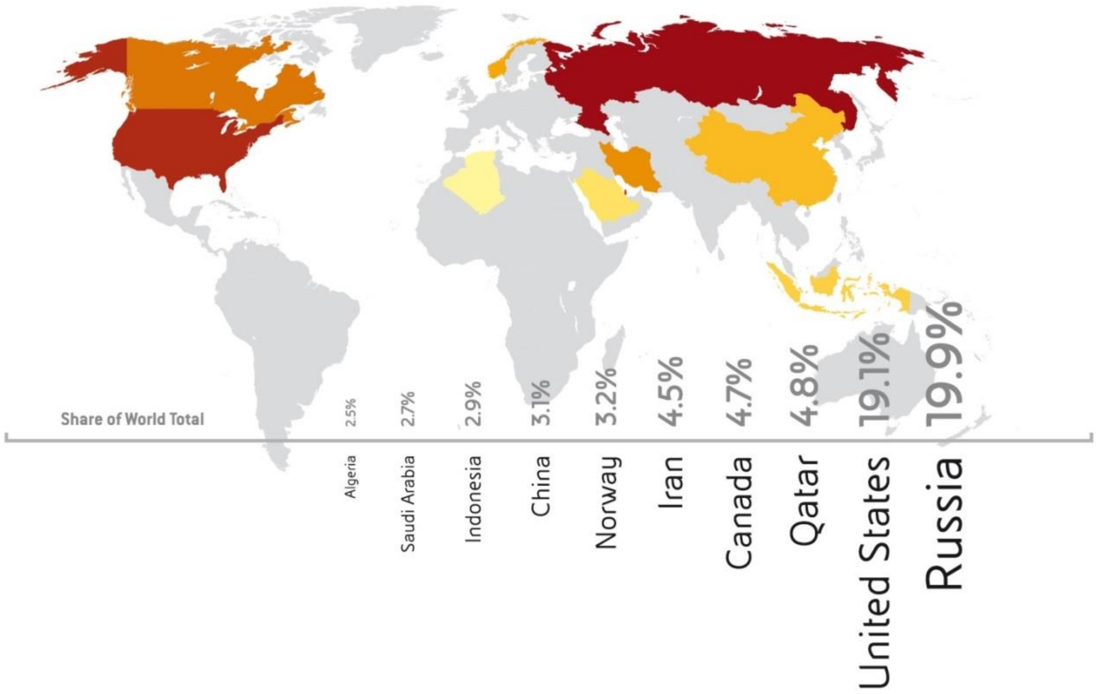
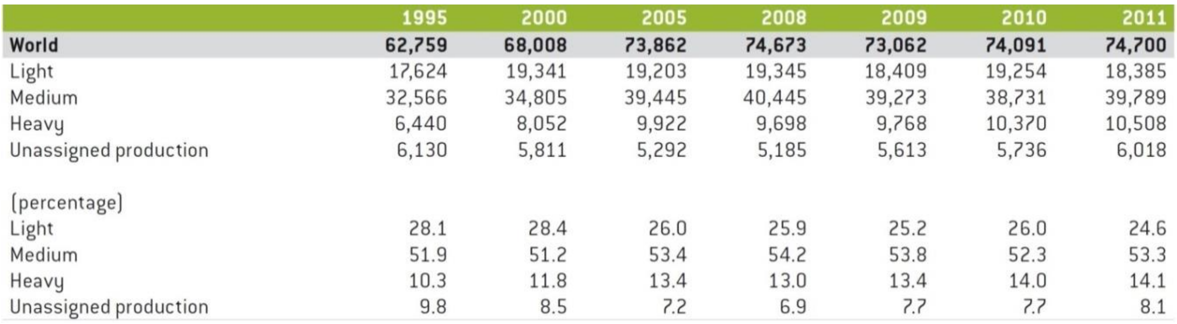


Figure 44 *The world top 10 natural gas producers (Eni, 2012)*

Table 21 *Crude production by gravity (thousand barrels/day) (Eni, 2012)*



	1995	2000	2005	2008	2009	2010	2011
World	**62,759**	**68,008**	**73,862**	**74,673**	**73,062**	**74,091**	**74,700**
Light	17,624	19,341	19,203	19,345	18,409	19,254	18,385
Medium	32,566	34,805	39,445	40,445	39,273	38,731	39,789
Heavy	6,440	8,052	9,922	9,698	9,768	10,370	10,508
Unassigned production	6,130	5,811	5,292	5,185	5,613	5,736	6,018
(percentage)							
Light	28.1	28.4	26.0	25.9	25.2	26.0	24.6
Medium	51.9	51.2	53.4	54.2	53.8	52.3	53.3
Heavy	10.3	11.8	13.4	13.0	13.4	14.0	14.1
Unassigned production	9.8	8.5	7.2	6.9	7.7	7.7	8.1

Table 22 *Crude production by sulfur content (thousand barrels/day) (Eni, 2012)*

	1995	2000	2005	2008	2009	2010	2011
World	**62,759**	**68,008**	**73,862**	**74,673**	**73,062**	**74,091**	**74,700**
Sweet	20,395	22,334	23,325	23,252	22,892	23,637	22,539
Medium Sour	4,946	6,042	6,593	8,225	8,477	8,681	8,757
Sour	31,288	33,821	38,653	38,010	36,080	36,036	37,386
Unassigned production	6,130	5,811	5,292	5,185	5,613	5,736	6,018
(percentage)							
Sweet	32.5	32.8	31.6	31.1	31.3	31.9	30.2
Medium Sour	7.9	8.9	8.9	11.0	11.6	11.7	11.7
Sour	49.9	49.7	52.3	50.9	49.4	48.6	50.0
Unassigned production	9.8	8.5	7.2	6.9	7.7	7.7	8.1

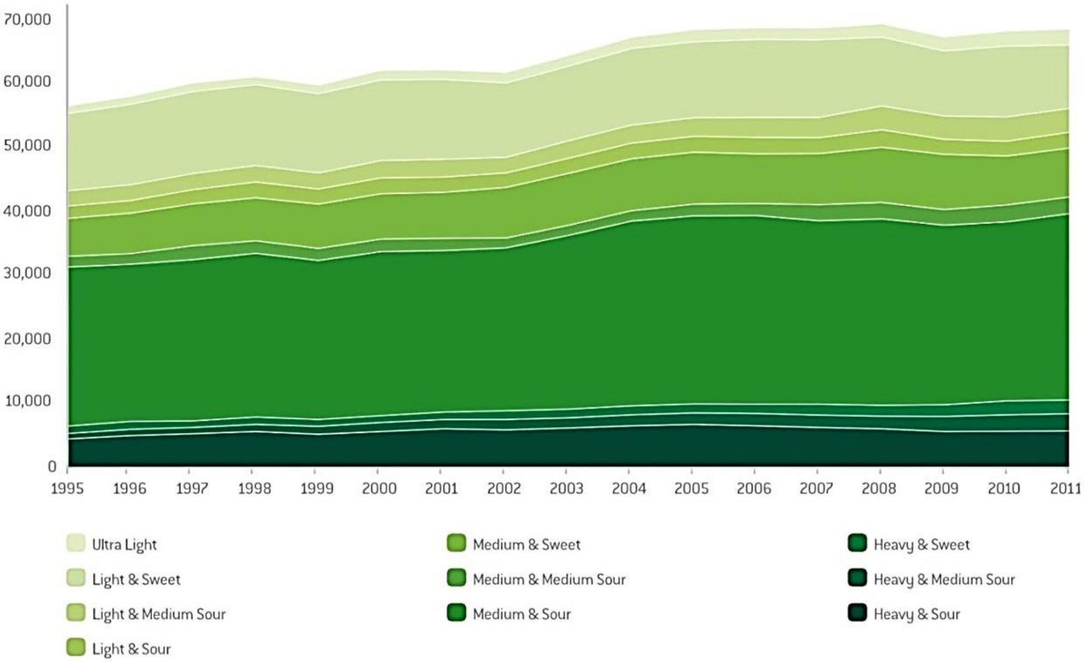


Figure 45 *Worldwide crude production by quality (thousand barrels/day) (Eni, 2012)*

Table 23 *Main features of some qualities of crude oil (benchmarks in* ***bold)*** *(Maugeri, 2006)*

Name	Origin	Daily production (thousand barrels)	API degree	Sulfur content (%)
Brent blend	**United Kingdom**	**300**	**38.7**	**0.31**
Forties	United Kingdom	650	37.3	0.40
Ekofisk	Norway	500	37.8	0.22
Statfjord	Norway	480	37.7	0.29
WTI Blend	**United States**	**300**	**38.7**	**0.45**
Alaskan North Slope	United States	950	31	1
Light Louisiana	United States	400	38.7	0.13
West Texas Sour	United States	775	34.2	1.30
BCF-17	Venezuela	800	16.5	2.5
Maya	Mexico	2,450	21.6	3.6
Isthmus	Mexico	500	32.8	1.4
Olmeca	Mexico	400	39.3	0.8
Urals	Russia	3,200	32	1.30
Siberian Light	Russia	100	35.6	0.46
Arabian Light	**Saudi Arabia**	**5,000**	**33.4**	**1.80**
Arabian Extra Light	Saudi Arabia	1,200	37	1.33
Arabian Medium	Saudi Arabia	1,500	30.3	2.45
Arabian Heavy	Saudi Arabia	800	28.7	2.8
Basrah Light	Iraq	1,600	30.2	2.6
Kirkuk	Iraq	350	33.3	2.3
Iran Heavy	Iran	1,700	30	2
Iran Light	Iran	1,300	33.4	1.6
Kuwait	Kuwait	2,000	31	2.63
Dubai	**Dubai**	**100**	**31.4**	**2**
Bonny Light	**Nigeria**	**450**	**34.3**	**0.15**
Forcados	Nigeria	400	30.4	0.18
Escavros	Nigeria	300	34.4	0.15
Cabina	Angola	300	32	0.12
Palanca	Angola	200	37	0.17
Brega	Libya	120	42	0.20
Bu Attifel	Libya	100	43	0.03
Es Sider	Libya	300	36.6	0.42
Saharan Blend	Algeria	350	47	0.11
Tapis	**Malaysia**	**300**	**45.2**	**0.03**
Daquing	China	1,000	32.2	0.09
Shengli	China	550	26	0.76

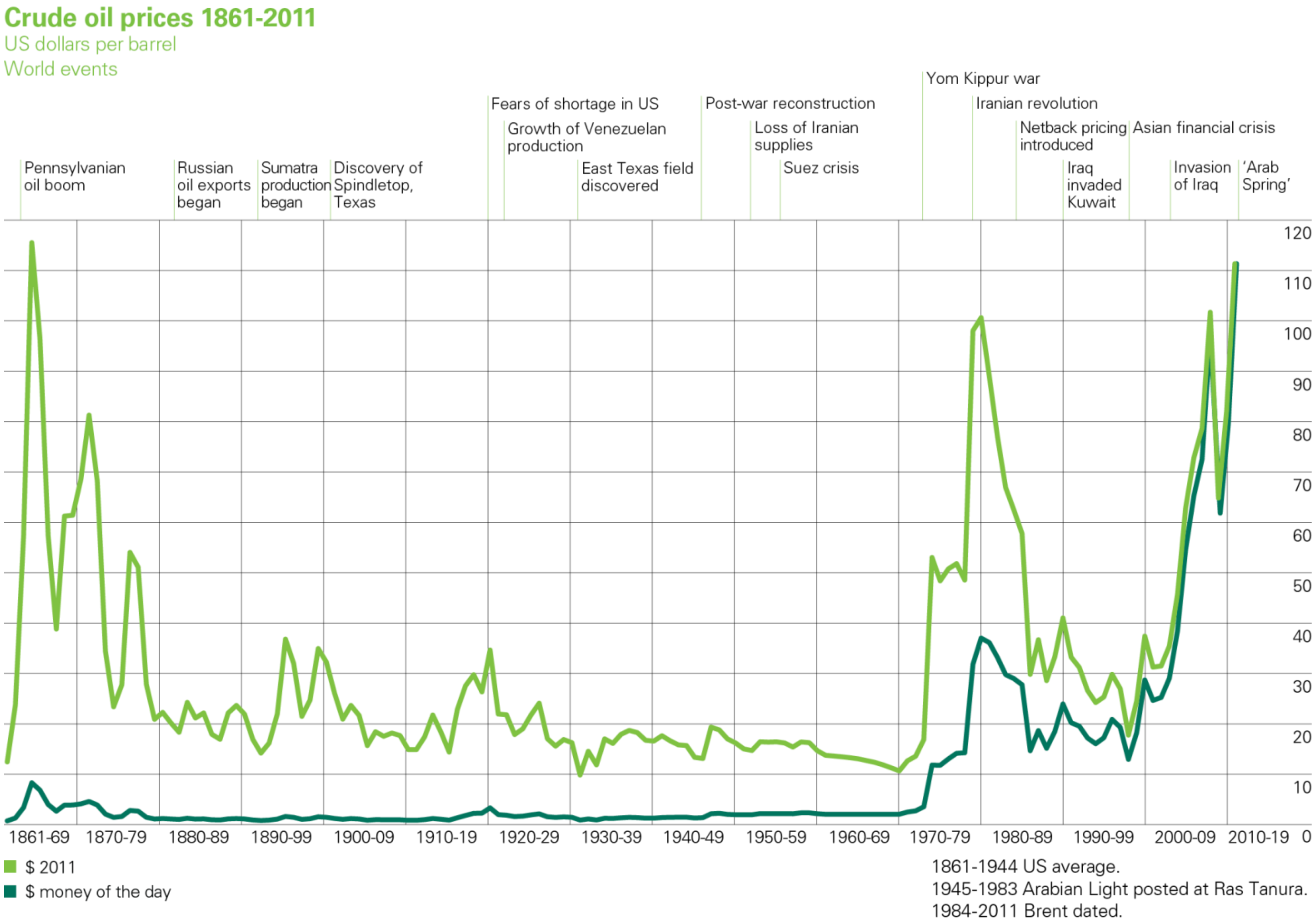


***Figure 46** Historical crude oil prices, 1861-2011 (BP, 2012)*

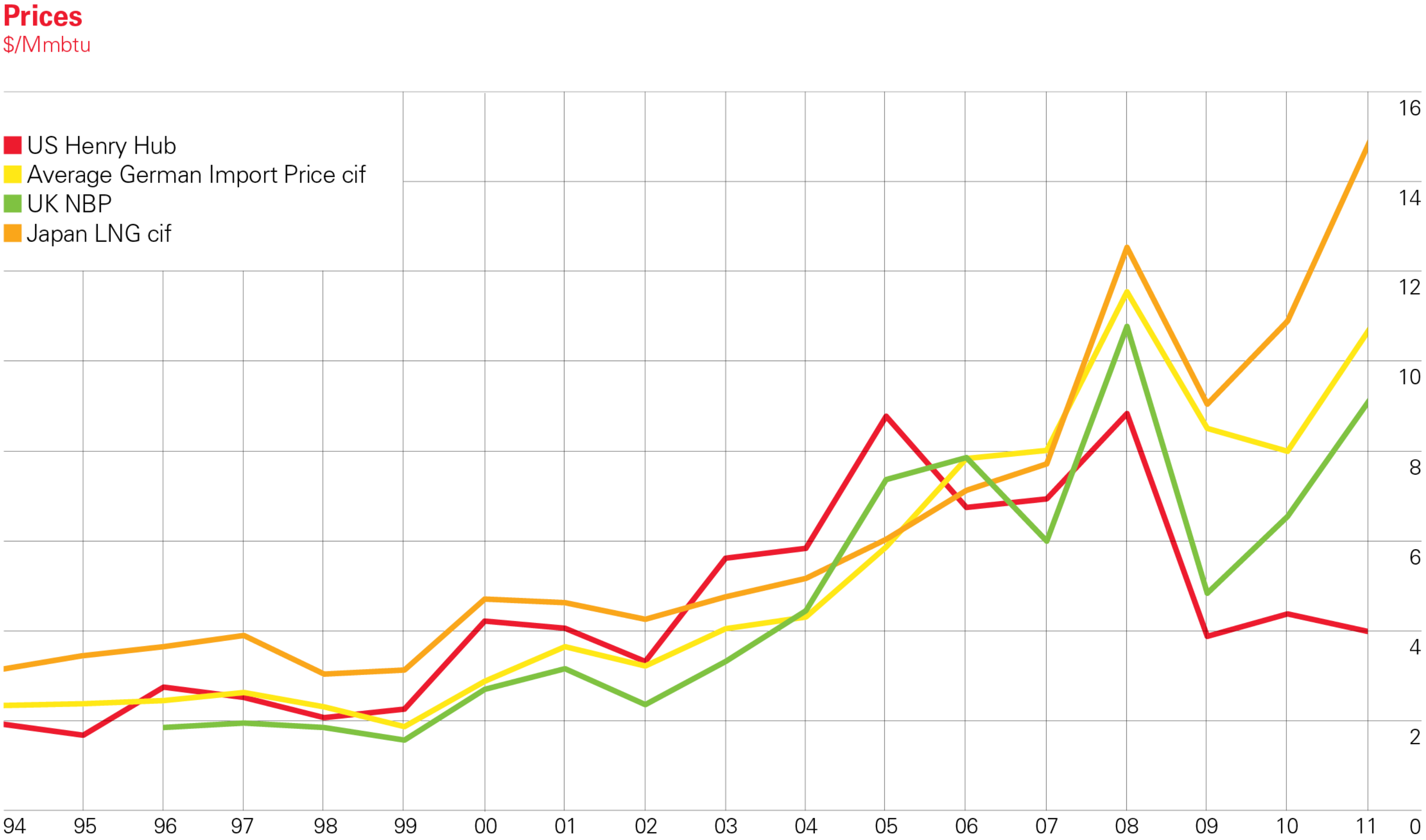


Figure 47 *Historical natural gas prices, 1994-2011 (BP, 2012)*

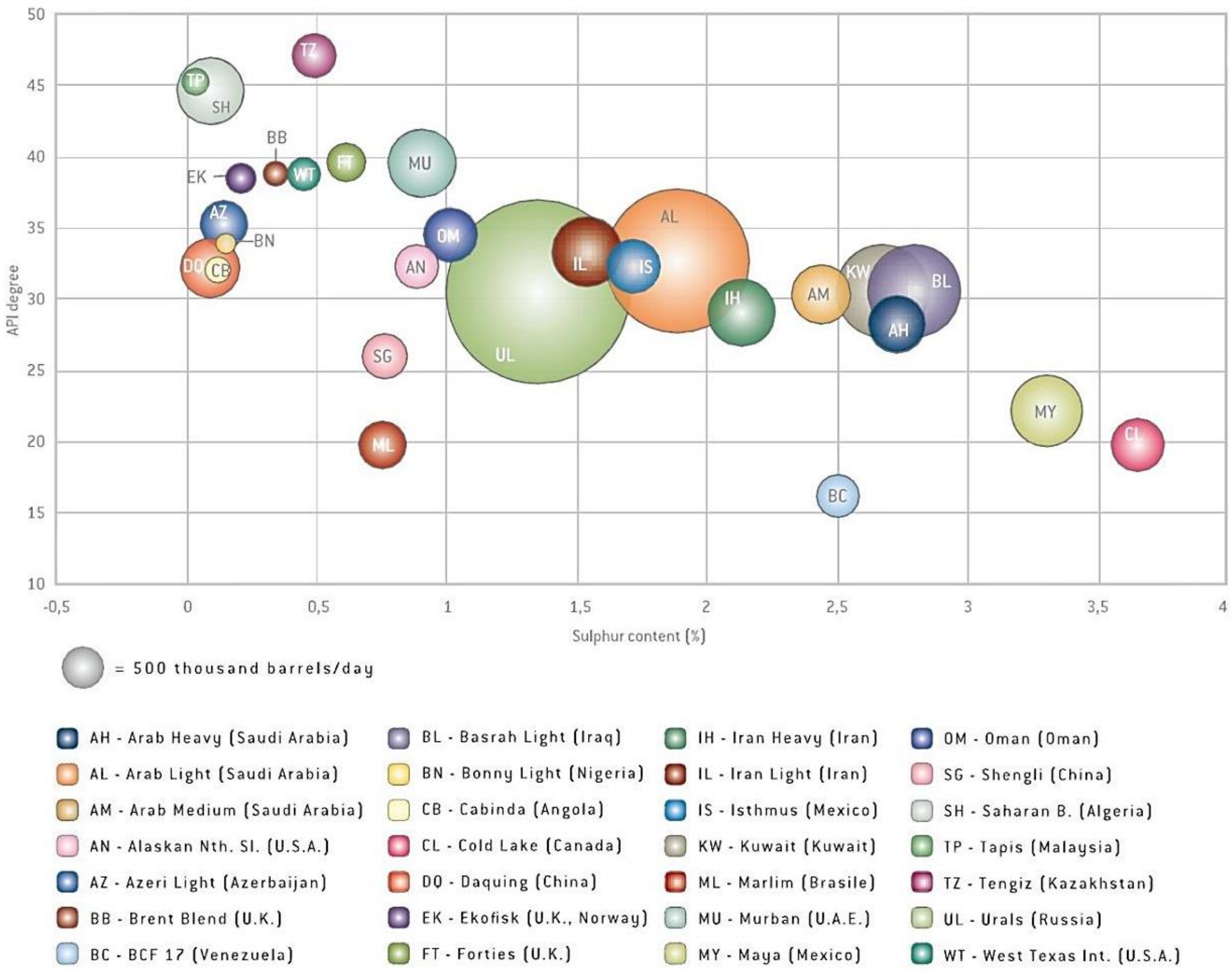


Figure 48 *Quality and production volume of main crudes (thousand barrels/day) (Eni, 2011)*

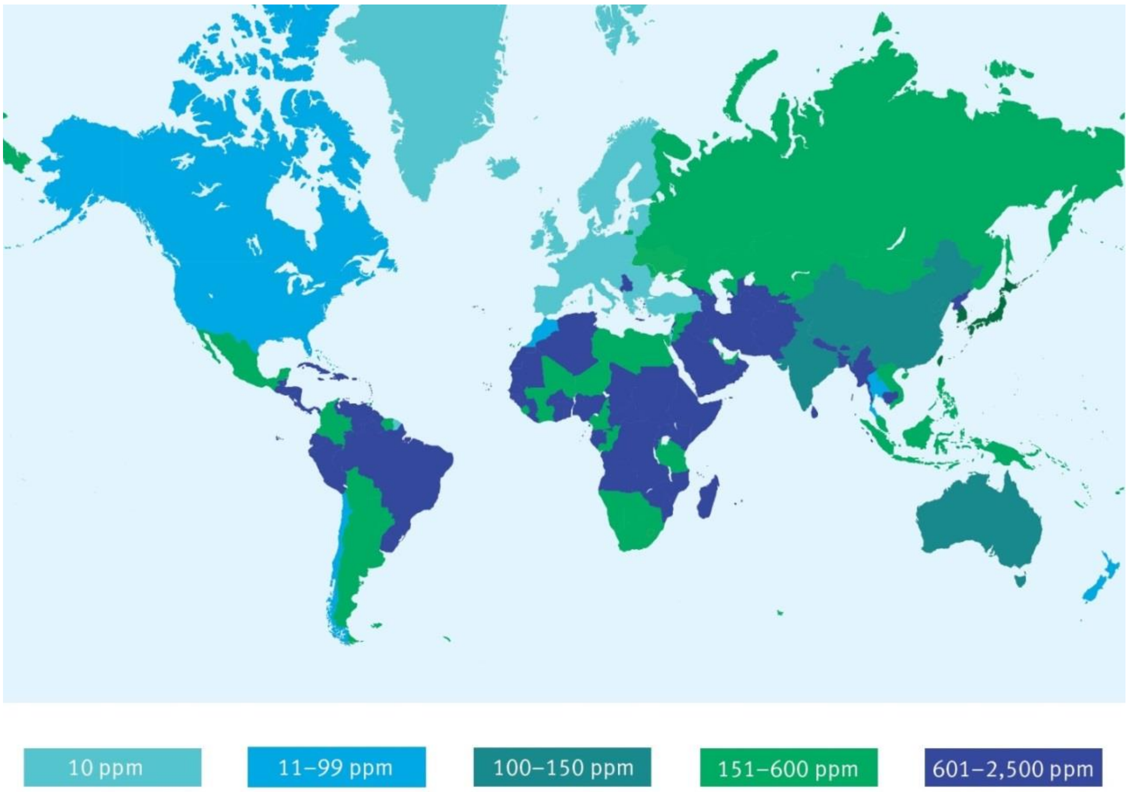


Figure 49 *Maximum gasoline sulfur limits as of September 2012 (OPEC, 2012)*

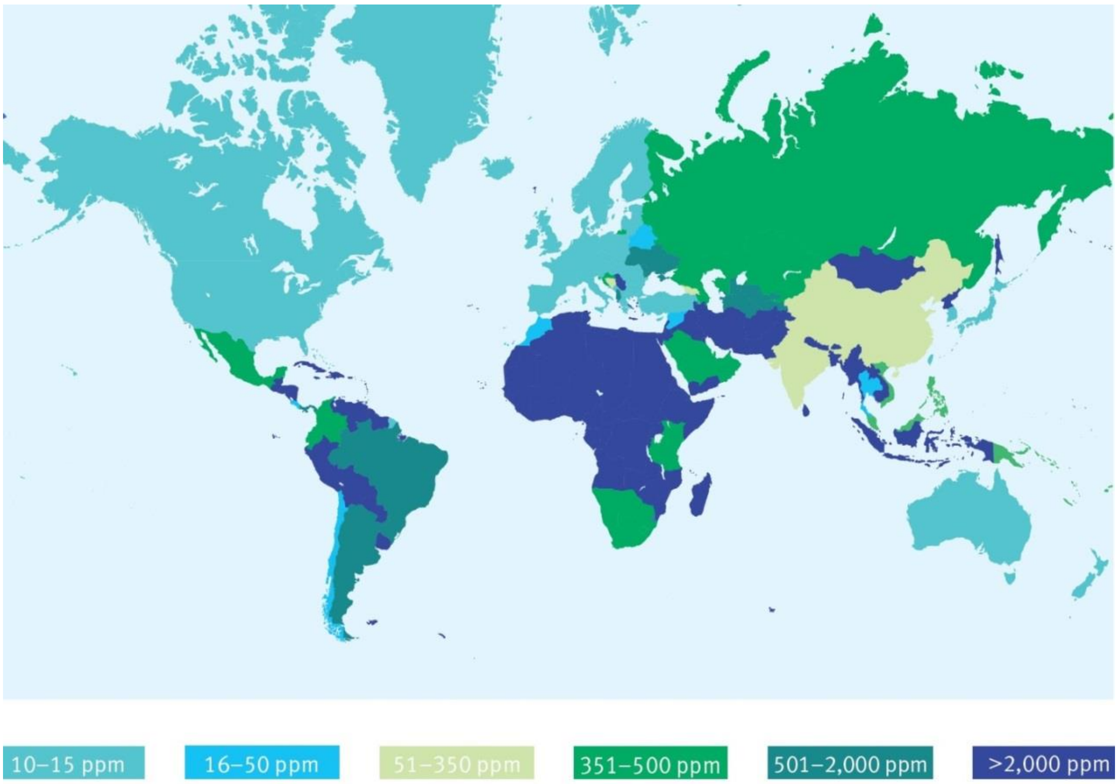


Figure 50 *Maximum on-road diesel sulfur limits as of September 2012 (OPEC, 2012)*

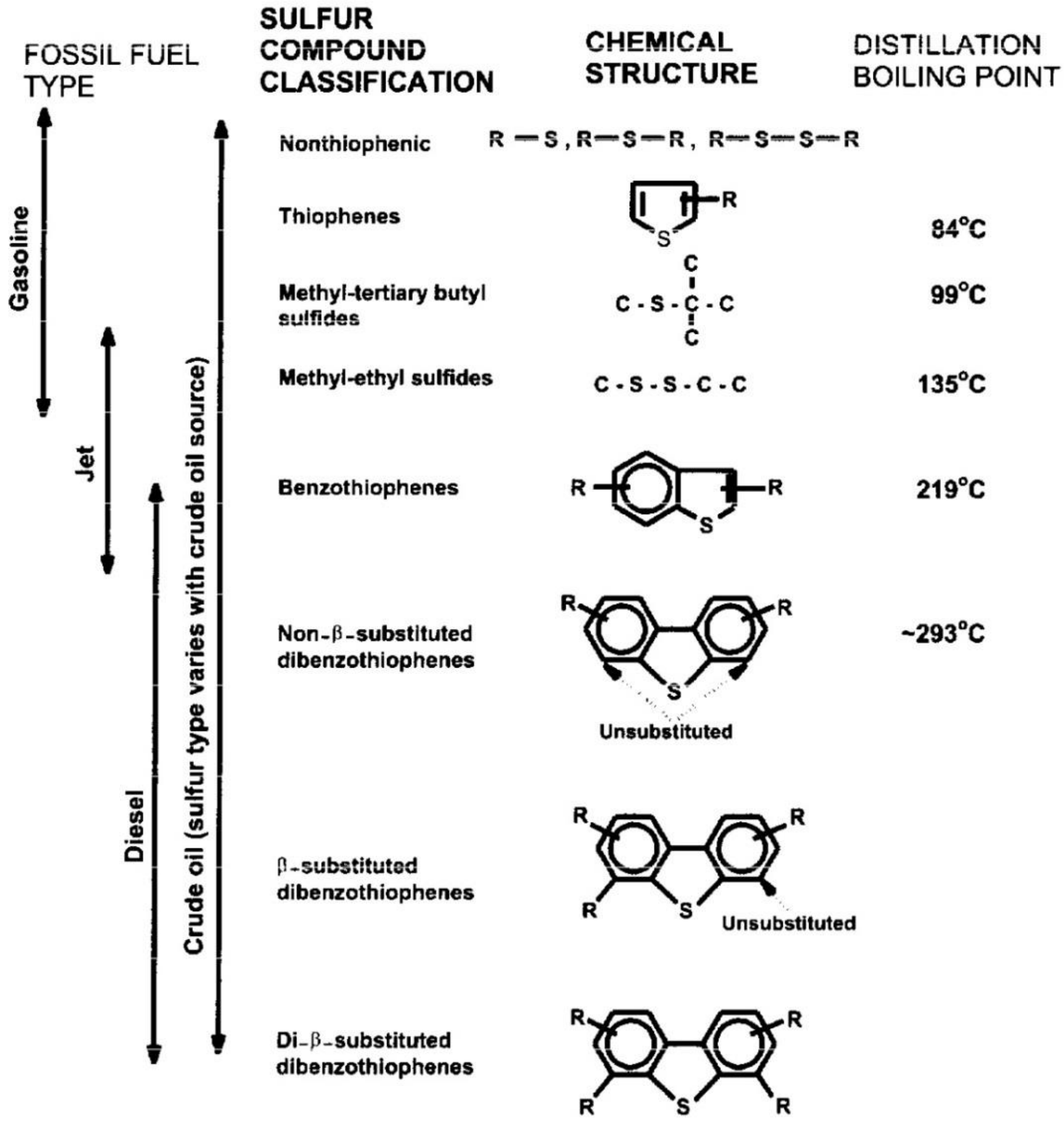


***Figure 51** Examples of organosulfur compounds present in fossil fuels (McFarland, 1999)*

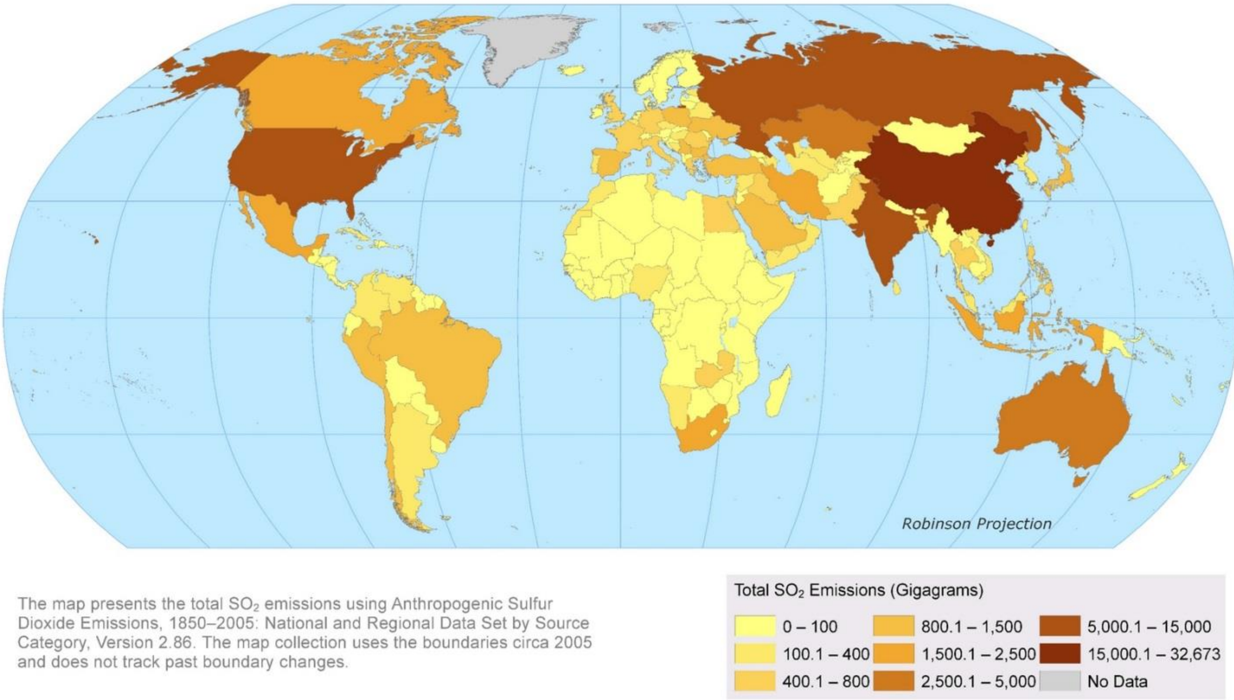
Table 24 *Effect of hydrotreatment on the characteristics of gas oil (Wauquier, 1995)*

Product designation	A	A+	A++	A+++	A++++
Density, kg/l at 15˚C	0.862	0.850	0.849	0.838	0.827
Viscosity at 20˚C, mm^2/s	5.55	5.34	5.22	5.12	4.90
Sulfur content, ppm	11,600	640	230	22	4
Nitrogen content, ppm	216	150	135	17	0.2
Cetane number	49.0	50.4	49.0	53.9	60.2
Composition, weight %					
Paraffins	36.5	36.2	36.8	37.0	41.4
Naphthenes	24.3	24.5	36.5	37.7	51.8
Monoaromatics	14.2	23.1	21.9	20.2	6.0
Diaromatics	15.4	12.8	12.6	4.5	0.8
Triaromatics	1.8	1.0	0.9	0.4	0.0
Thiophenes	7.7	2.4	1.4	0.3	0.0
Total aromatics	39.1	39.3	36.8	25.4	6.8

Table 25 *Overview of petroleum refining processes (OSHA, 1999)*

Process name	Action	Method	Purpose	Feedstock	Product
Fractional processes					
Atmospheric distillation	Separation	Thermal	Separate fractions	Desalted crude oil	Gas, gas oil, distillate, residual
Vacuum distillation	Separation	Thermal	Separate w/o cracking	Atmospheric tower residua	Gas oil, lube stock, residual
Conversion processed-decomposition					
Catalytic cracking	Alteration	Catalytic	Upgrade gasoline	Gas oil, coke distillate	Gasoline, petrochemical feedstock
Coking	Polymerize	Thermal	Convert vacuum residuals	Gas oil, coke distillate	Gasoline, petrochemical feedstock
Hydro-cracking	Hydrogenate	Catalytic	Convert to lighter HC's	Gas oil, cracked oil, residual	Lighter, higher-quality products
Visbreaking	Decompose	Thermal	Reduce viscosity	Atmospheric tower residual	Distillate, tar
Conversion processes-unification					
Alkylation	Combining	Catalytic	Unite olefins & isoparaffins	Tower isobutane/ cracker olefin	Iso-octane (alkylate)
Grease compounding	Combining	Thermal	Combine soaps & oils	Lube oil, fatty acid, alky metal	Lubricating grease
Polymerizing	Polymerize	Catalytic	Unite 2 or more olefins	Cracker olefins	High-octane naphtha, petrochemical stocks
Conversion processes-alteration or rearrangement					
Catalytic reforming	Alteration/ dehydration	Catalytic	Upgrade low-octane naphtha	Coker/ hydro-cracker naphtha	High octane reformate/ aromatic

Isomerization	Rearrange	Catalytic	Convert straight chain to branch	Butane, pentane, hexane	Isobutane/ pentane/ hexane
Treatment processes					
Amine treating	Treatment	Absorption	Remove acidic contaminants	Sour gas, HCs w/CO_2 & H_2S	Acid free gases & liquid HCs
Desalting	Dehydration	Absorption	Remove contaminants	Crude oil	Desalted crude oil
Drying & sweetening	Treatment	Absorption /thermal	Remove H_2O & sulfur compounds	Liquid HCs, LPG, alkyl feedstock	Sweet & dry hydrocarbons
Furfural extraction	Solvent extraction	Absorption	Upgrade mid distillate & lubes	Cycle oils & lube feed-stocks	High quality diesel & lube oil
Hydrodesulphurization	Treatment	Catalytic	Remove sulfur, contaminants	High-sulfur residual/ gas oil	Desulfurized olefins
Hydrotreating	Hydrogenation	Catalytic	Remove impurities, saturate HC's	Residuals, cracked HC's	Cracker feed, distillate, lube
Phenol extraction	Solvent extraction	Absorption /thermal	Improve viscosity index, color	Lube oil base stocks	High quality lube oils
Solvent deasphalting	Treatment	Absorption	Remove asphalt	Vacuum tower residual, propane	Heavy lube oil, asphalt
Solvent dewaxing	Treatment	Cool/ filter	Remove wax from lube stocks	Vacuum tower lube oils	Dewaxed lube basestock
Solvent extraction	Solvent extraction	Absorption/ precipitation	Separate unsat. oils	Gas oil, reformate, distillate	High-octane gasoline
Sweetening	Treatment	Catalytic	Remove H_2S, convert mercaptan	Untreated distillate/gasoline	High-quality distillate/gasoline



The map presents the total SO_2 emissions using Anthropogenic Sulfur Dioxide Emissions, 1850–2005: National and Regional Data Set by Source Category, Version 2.86. The map collection uses the boundaries circa 2005 and does not track past boundary changes.

Figure 52 *Worldwide total SO_2 emissions as of 2005 (NASA, 2005)*

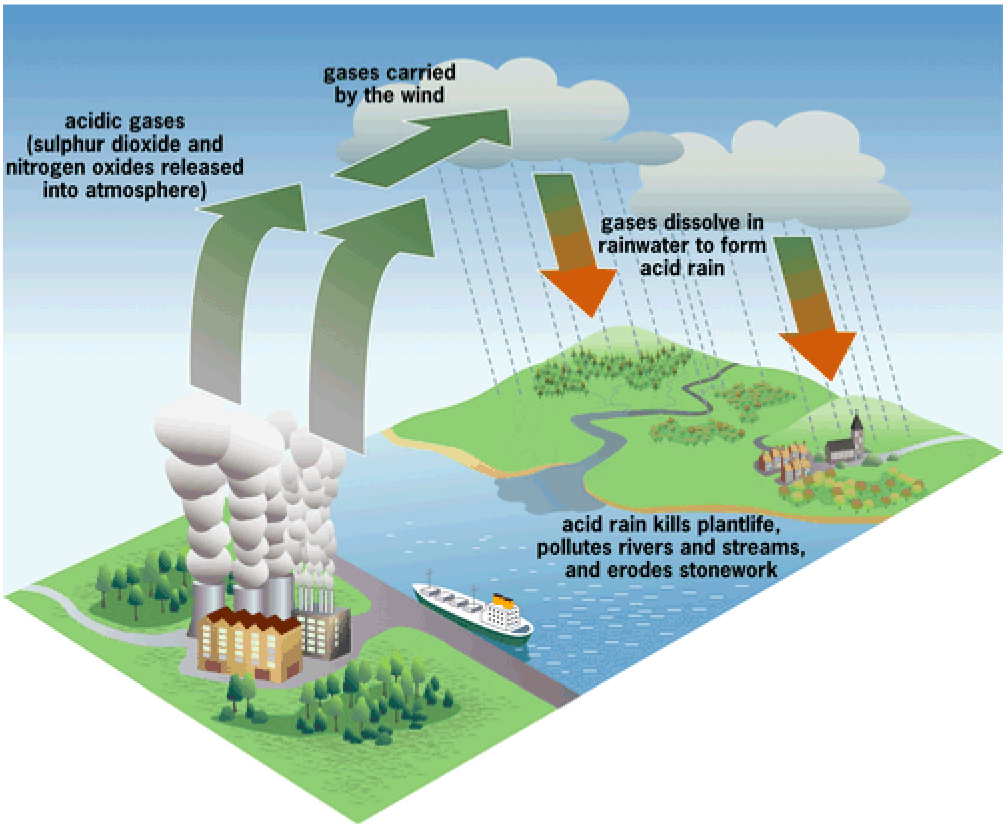


Figure 53 *Acid rain formation (McDonald, 2009)*