

# 8 PETROLEUM

## Abstract

Petroleum dominates the world economy. No other commodity affects everyday life the way petroleum does. Although more than 70% of petroleum is used for transportation, it is an essential raw material for making a variety of products that we use in our everyday life. Petroleum is a complex chemical mixture and its trade and also processing depend on its physical and chemical properties. Crude petroleum pumped out from the underground reservoirs goes through a number of processing steps before the final products are obtained and sold to the public. The main objective of the processing is to maximize the yield of transportation fuels. Exploration, extraction from underground reservoirs, benchmarking and processing of crude petroleum are discussed in this chapter.

## 8.1 Introduction

The word “petroleum” comes from the Latin words *petra*, (or rock), and *oleum*, (oil). Oil is found in reservoirs in sedimentary rocks. Tiny pores in the rock allowed the petroleum to seep in. These “reservoir rocks” hold the oil like a sponge, confined by other non-porous layers that form a “trap.”

According to the most widely accepted theory, oil is composed mainly of hydrocarbons, and was formed millions of years ago in a process that began when aquatic plant and animal remains were covered by layers of sediment – particles of rock and mineral. Over millions of years of extreme pressure and high temperatures, these particles became the mix of liquid hydrocarbons that we know as oil. Different mixes of plant and animal remains, as well as pressure, heat, and time, have caused hydrocarbons to appear today in a variety of forms: crude oil, a liquid; natural gas, a gas; and coal, a solid. Although the major consumption of oil is in transportation sector, as can be seen from Table 8.1, petroleum or oil is the key raw material for a variety of other consumer products.

**Table 8.1.** Products that use petroleum as the starting raw material for their manufacturing.

<b>Commercial products</b>			
Ink	Dishwashing liquids	Paint brushes	Cameras
Telephones	Toys	Unbreakable dishes	Combs
Insecticides	Antiseptics	Dolls	Dice
Car sound	insulation	Fishing lures	Mops
Deodorant	Tires	Motorcycle helmets	Purses
Linoleum	Sweaters	Tents	Dresses
Refrigerator	linings	Paint rollers	Pajamas
Floor wax	Shoes	Electrician's tape	Pillows
Plastic wood	Model cars	Glue	Candles
Roller-skate	wheels	Trash bags	Ice buckets
Hand Lotion	Clothesline	Dyes	Crayons
Soft contact lenses	Shampoo	Panty hose	Caulking
Food preservatives	Fishing rods	Oil filters	Life jackets
Transparent tape	Anesthetics	Upholstery	Garden hose
Disposable diapers	TV cabinets	Cassettes	Plywood adhesive
Sports car bodies	Salad bowls	House paint	Milk jugs
Electric blankets	Awnings	Ammonia	Sun glasses
Car battery cases	Safety glass	Hair curlers	Cold cream
Synthetic rubber	VCR tapes	Eyeglasses	Antihistamines
Vitamin capsules	Movie film	Ice chests	Slacks
Rubbing alcohol	Loudspeakers	Fertilizers	False teeth
Ice cube trays	Credit cards	Toilet seats	Toothpaste
Insect repellent	Water pipes	Toothbrushes	Golf balls
Roofing shingles	Fishing boots	Wire insulation	Cortisone
Balloons	Shower curtains	Fan belts	Artificial limbs
Umbrellas	Curtains	Heart valves	Parachutes
Beach umbrellas	Detergents	Aspirin	Faucet washers
Putty	Rubber cement	Bandages	Tool racks
Hair coloring	Nail polish	Guitar strings	Tennis rackets
Drinking cups	Petroleum jelly	Luggage	Shoe polish
Yarn	Shower doors	Artificial turf	Lipstick
Golf bags	Vaporizers	Wading pools	Perfume
Roofing	Folding doors	Ballpoint pens	Carpeting
LP records	Hearing aids	Shaving cream	Soap dishes
Skis	Permanent press clothes	Soap dishes	

## 8.2 Consumption of Oil

No other commodity dominates modern society in the way the oil does. Oil not only drives the global economy, it also controls our life style. Table 8.2 shows the oil consumption by various countries. World oil consumption increased by 2% in 2003, followed by a 4% increase in 2004. The 4% rise in 2004 was the largest yearly increase in a quarter-century. This sudden unexpected increase in oil consumption in 2004 year was due to the rapid growth of oil use in the United States and East Asia, notably China. In 2005, growth of world oil consumption slowed to 1.5%, partly reflecting the restraining effects of higher prices. Nonetheless, the level of oil consumption is still high relative to earlier expectations. The demand is expected to remain strong because its consumption is directly related to the global economy. As can be seen from the table, although the consumption of oil in the USA decreased in 2005, the world consumption increased by 1%. The worldwide crude oil demand for 2006 was estimated to be around 84.83 million barrels a day, or a growth of about 1.5%. Most of the increase in the output came from the OPEC (Organization of the Petroleum Exporting Countries) who pumped additional 170,000 barrels a day in April, increasing its output to 30.04 million barrels a day.

**Table 8.2.** Oil consumption by the countries (million barrels per day).

	Year					Change 2006 over 2005	2006 share of total
	2002	2003	2004	2005	2006		
USA	19,761	20,033	20,731	20,802	20,589	-1.3%	24.1%
Canada	2,067	2,132	2,248	2,247	2,222	-1.5%	2.5%
Mexico	1,837	1,885	1,919	1,973	1,972	-0.8%	2.2%
Total North America	23,665	24,050	24,898	25,023	24,783	-1.3%	28.9%
Argentina	364	372	394	421	442	5.1%	0.5%
Brazil	2,063	1,985	1,999	2,047	2,097	2.2%	2.4%
Chile	228	229	229	244	248	1.8%	0.3%
Colombia	222	222	223	225	230	2.7%	0.3%
Ecuador	131	137	141	168	180	7.3%	0.2%
Peru	147	140	151	165	160	-3.9%	0.2%
Venezuela	594	479	518	547	565	3.4%	0.7%
Other S. & Cent. America	1,144	1,160	1,170	1,189	1,230	3.4%	1.5%
Total S. & Cent. America	4,892	4,725	4,826	5,006	5,152	2.9%	6.1%
Austria	271	293	285	295	294	-0.2%	0.4%
Azerbaijan	74	86	92	107	96	-10.7%	0.1%

(Continued)

Table 8.2. (Continued)

	Year					Change 2006 over 2005	2006 share of total
	2002	2003	2004	2005	2006		
Belgium & Luxembourg	691	748	785	815	837	2.8%	1.1%
Bulgaria	88	103	103	108	110	1.4%	0.1%
Czech Republic	174	185	203	211	208	-1.1%	0.3%
Denmark	200	193	189	195	201	3.1%	0.2%
Finland	226	239	224	233	225	-4.0%	0.3%
France	1,967	1,965	1,978	1,960	1,952	-0.3%	2.4%
Germany	2,714	2,664	2,634	2,605	2,622	0.9%	3.2%
Greece	414	404	435	432	451	4.7%	0.6%
Hungary	140	132	136	159	160	1.1%	0.2%
Iceland	19	18	20	21	20	-5.5%	-
Republic of Ireland	182	178	185	196	195	-0.6%	0.2%
Italy	1,943	1,927	1,873	1,819	1,793	-1.1%	2.2%
Kazakhstan	193	183	188	208	221	6.0%	0.3%
Lithuania	53	51	55	58	59	0.4%	0.1%
Netherlands	952	962	1,003	1,070	1,057	w	1.3%
Norway	208	219	210	212	217	2.9%	0.3%
Poland	420	435	460	479	502	5.4%	0.6%
Portugal	338	317	322	331	344	4.9%	0.4%
Romania	226	199	230	223	223	-0.4%	0.3%
Russian Federation	2,606	2,622	2,634	2,628	2,735	4.2%	3.3%
Slovakia	76	71	68	81	82	2.8%	0.1%
Spain	1,526	1,559	1,593	1,619	1,602	-0.9%	2.0%
Sweden	317	332	319	315	312	-0.9%	0.4%
Switzerland	267	259	258	262	269	2.5%	0.3%
Turkey	656	668	688	649	617	-4.7%	0.7%
Turkmenistan	86	95	103	110	117	6.3%	0.1%
Ukraine	278	286	293	294	317	8.1%	0.4%
United Kingdom	1,693	1,717	1,764	1,802	1,781	-1.0%	2.1%
Uzbekistan	130	148	134	139	143	3.0%	0.2%
Other Europe & Eurasia	453	495	518	540	558	3.1%	0.7%
Total Europe & Eurasia	19,726	19,905	20,132	20,314	20,482	1.1%	24.9%
Iran	1,429	1,513	1,575	1,607	1,669	3.7%	2.0%
Kuwait	222	238	266	302	275	-10.4%	0.4%
Qatar	79	77	84	98	110	15.0%	0.1%
Saudi Arabia	1,572	1,684	1,805	1,891	2,005	6.2%	2.4%
United Arab Emirates	320	333	355	376	408	7.8%	0.5%
Other Middle East	1,425	1,393	1,407	1,437	1,455	1.2%	1.8%
Total Middle East	5,047	5,238	5,492	5,712	5,923	3.5%	7.2%
Algeria	222	231	240	251	260	4.3%	0.3%
Egypt	534	550	567	623	612	-2.4%	0.7%

	Year					Change 2006 over 2005	2006 share of total
	2002	2003	2004	2005	2006		
South Africa	499	512	523	494	499	0.6%	0.6%
Other Africa	1,254	1,274	1,314	1,362	1,419	4.2%	1.7%
Total Africa	2,510	2,567	2,645	2,731	2,790	2.0%	3.4%
Australia	846	851	854	848	886	4.5%	1.0%
Bangladesh	80	83	83	84	86	1.7%	0.1%
China	5,288	5,803	6,772	6,984	7,445	6.7%	9.0%
China Hong Kong SAR	268	269	314	285	273	-4.3%	0.3%
India	2,374	2,420	2,573	2,569	2,575	0.6%	3.1%
Indonesia	1,115	1,132	1,150	1,168	1,031	-11.9%	1.3%
Japan	5,359	5,455	5,281	5,355	5,164	-3.7%	6.0%
Malaysia	489	480	493	477	499	4.6%	0.6%
New Zealand	141	148	150	154	156	1.6%	0.2%
Pakistan	357	321	325	353	372	5.9%	0.5%
Philippines	332	330	336	314	307	-1.9%	0.4%
Singapore	699	668	748	794	853	7.8%	1.1%
South Korea	2,282	2,300	2,283	2,308	2,312	-0.1%	2.7%
Taiwan	999	1,069	1,084	1,113	1,120	0.7%	1.3%
Thailand	766	836	913	918	926	0.7%	1.1%
Other Asia Pacific	504	509	546	571	584	2.0%	0.7%
Total Asia Pacific	21,898	22,674	23,905	24,294	24,589	1.3%	29.5%
<b>TOTAL WORLD</b>	<b>77,737</b>	<b>79,158</b>	<b>81,898</b>	<b>83,080</b>	<b>83,719</b>	<b>0.7%</b>	<b>100.0%</b>
European Union 25 #	14,471	14,546	14,686	14,861	14,865	0.3%	18.2%
European Union 27 #	14,785	14,849	15,019	15,192	15,198	0.3%	18.6%
OECD	47,687	48,289	49,095	49,448	49,041	-0.9%	58.1%
Former Soviet Union	3,667	3,748	3,783	3,819	3,997	4.7%	4.8%
Other EMEs	26,383	27,121	29,021	29,812	3,0682	2.9%	37.1%

OECD-Organization for Economic Co-operation and Development; EME-Established Market Economy

\* Inland demand plus international aviation and marine bunkers and refinery fuel and loss. Consumption of fuel ethanol and biodiesel is also included

^ Less than 0.5; w Less than 0.05%.

# Excludes Estonia, Latvia and Lithuania prior to 1985 and Slovenia prior to 1991.

Annual changes and shares of total are calculated using million tonnes per annum figures. Differences between these world consumption figures and world production statistics are accounted for by stock changes, consumption of non-petroleum additives and substitute fuels, and unavoidable disparities in the definition, measurement or conversion of oil supply and demand data.

Source: Reference [1].

World oil production has been able to meet the consumption so far. The increase in production came mainly from the OPEC countries. However, as shown in Table 8.3, the oil production of a number of oil exporting countries is declining. World oil demand is expected to grow from 84.83 million barrels per day in 2006 to 98 million barrels per day in 2015 and 118 million barrels per day in 2030. This

increased demand will continue despite the increase in world oil prices that is expected to be 35% higher in 2025 than the current price. Much of the growth in oil consumption is projected for the nations of non-OECD (Organization for Economic Co-operation and Development) Asia, where strong economic growth is expected. Non-OECD Asia (including China and India) accounts for 43% of the total increase in world oil use over the projection period.

**Table 8.3.** Oil production by various countries in the last several years.

	Year					Change 2006 over 2005	2006 share of total
	2002	2003	2004	2005	2006		
USA	7,626	7,400	7,228	6,895	6,871	-0.5%	8.0%
Canada	2,858	3,004	3,085	3,041	3,147	4.4%	3.9%
Mexico	3,585	3,789	3,824	3,760	3,683	-2.1%	4.7%
Total North America	14,069	14,193	14,137	13,695	13,700	0.1%	16.5%
Argentina	818	806	754	725	716	-1.3%	0.9%
Brazil	1,499	1,555	1,542	1,715	1,809	5.5%	2.3%
Colombia	601	564	551	554	558	0.7%	0.7%
Ecuador	401	427	535	541	545	0.7%	0.7%
Peru	98	92	94	111	116	3.5%	0.1%
Trinidad & Tobago	155	164	152	171	174	1.5%	0.2%
Venezuela	2,895	2,554	2,907	2,937	2,824	-3.9%	3.7%
Other S. & Cent. America	152	153	144	142	140	-1.7%	0.2%
Total S. & Cent. America	6,619	6,314	6,680	6,897	6,881	-0.4%	8.8%
Azerbaijan	311	313	315	452	654	44.9%	0.8%
Denmark	371	368	390	377	342	-9.3%	0.4%
Italy	106	107	105	117	111	-5.6%	0.1%
Kazakhstan	1,018	1,111	1,297	1,356	1,426	5.6%	1.7%
Norway	3,333	3,264	3,188	2,969	2,778	-6.9%	3.3%
Romania	127	123	119	114	105	-8.0%	0.1%
Russian Federation	7,698	8,544	9,287	9,552	9,769	2.2%	12.3%
Turkmenistan	182	202	193	192	163	-15.2%	0.2%
United Kingdom	2,463	2,257	2,028	1,809	1,636	-9.6%	2.0%
Uzbekistan	171	166	152	126	125	-0.7%	0.1%
Other Europe & Eurasia	501	509	496	469	454	-2.9%	0.5%
Total Europe & Eurasia	16,281	16,965	17,570	17,533	17,563	0.2%	21.6%

	Year					Change	2006
	2002	2003	2004	2005	2006	2006 over 2005	share of total
Iran	3,543	4,183	4,248	4,268	4,343	1.2%	5.4%
Iraq	2,116	1,344	2,030	1,833	1,999	9.0%	2.5%
Kuwait	1,995	2,329	2,482	2,643	2,704	2.4%	3.4%
Oman	900	824	756	779	743	-4.6%	0.9%
Qatar	783	917	990	1,045	1,133	8.1%	1.3%
Saudi Arabia	8,928	10,164	10,638	11,114	10,859	-2.3%	13.1%
Syria	548	527	495	458	417	-8.9%	0.5%
United Arab Emirates	2,324	2,611	2,656	2,751	2,969	7.3%	3.5%
Yemen	457	448	420	426	390	-8.7%	0.5%
Other Middle East	48	48	48	34	32	-7.7%	w
Total Middle East	21,642	23,395	24,764	25,352	25,589	0.7%	31.2%
Algeria	1,680	1,852	1,946	2,016	2,005	-0.3%	2.2%
Angola	905	862	976	1,233	1,409	14.3%	1.8%
Cameroon	75	68	62	58	63	8.6%	0.1%
Chad	-	24	168	173	153	-11.7%	0.2%
Rep. of Congo (Brazzaville)	231	215	216	246	262	6.7%	0.3%
Egypt	751	749	721	696	678	-2.5%	0.8%
Equatorial Guinea	215	247	343	356	358	0.6%	0.5%
Gabon	295	240	235	234	232	-0.9%	0.3%
Libya	1,375	1,485	1,624	1,751	1,835	4.2%	2.2%
Nigeria	2,103	2,263	2,502	2,580	2,460	-4.9%	3.0%
Sudan	233	255	325	355	397	11.8%	0.5%
Tunisia	75	68	72	74	69	-7.1%	0.1%
Other Africa	63	71	75	72	68	-5.3%	0.1%
Total Africa	8,001	8,398	9,263	9,846	9,990	1.4%	12.1%
Australia	731	624	541	554	544	-2.1%	0.6%
Brunei	210	214	210	206	221	7.1%	0.3%
China	3,346	3,401	3,481	3,627	3,684	1.6%	4.7%
India	801	798	816	784	807	3.1%	1.0%
Indonesia	1,288	1,183	1,152	1,129	1,071	-5.3%	1.3%
Malaysia	757	776	793	767	747	-3.1%	0.9%
Thailand	204	236	223	265	286	8.7%	0.3%
Vietnam	354	364	427	398	367	-8.0%	0.5%

(Continued)

**Table 8.3.** (Continued)

	Year					Change	2006
	2002	2003	2004	2005	2006	2006 over 2005	share of total
Other Asia Pacific	193	195	186	197	215	8.0%	0.3%
Total Asia Pacific	7,884	7,791	7,829	7,926	7,941	0.1%	9.7%
<b>TOTAL WORLD</b>	<b>74,496</b>	<b>77,056</b>	<b>80,244</b>	<b>81,250</b>	<b>81,663</b>	<b>0.4%</b>	<b>100.0%</b>
European Union 25 #	3,203	2,995	2,774	2,535	2,306	-9.0%	2.8%
European Union 27 #	3,331	3,119	2,893	2,649	2,412	-8.9%	2.9%
OECD	21,422	21,156	20,716	19,825	19,398	-2.2%	23.3%
OPEC 11	29,031	30,884	33,175	34,068	34,202	0.2%	41.7%
OPEC 12	29,936	31,746	34,151	35,301	35,611	0.7%	43.5%
Non-OPEC £	35,933	35,673	35,661	35,343	35,162	-0.5%	43.0%
Former Soviet Union	9,533	10,499	11,407	11,840	12,299	3.9%	15.3%

\* Includes crude oil, shale oil, oil sands and NGLs ( the liquid content of natural gas where this is recovered separately). Excludes liquid fuels from other sources such as biomass and coal derivatives.

^ Less than 0.05; w Less than 0.05%; # Excludes Estonia, Latvia and Lithuania prior to 1985 and Slovenia prior to 1991; £ Excludes Former Soviet Union, includes Angola.

Annual changes and shares of total are calculated using million tonnes per annum figures.

Source: Reference [1].

On the supply side, the production of oil has been constrained by available capacity, natural disasters, and geopolitical developments. In 2003 and 2004, as oil consumption and prices rose briskly, Saudi Arabia and other members of OPEC pumped more oil. OPEC was able to boost production relatively quickly in response to changing market conditions by utilizing production capacity that had been idle. By the end of 2004, however, OPEC's spare production capacity was greatly diminished (Fig. 8.1). As a consequence, OPEC's oil production flattened out over the past year even as oil prices continued to soar. Oil production outside OPEC also leveled off last year, contrary to earlier expectations for continued growth. The projected excess oil production capacity of the world is shown in Fig. 8.2

OPEC has maintained excess capacity of only 1 million to 2 million barrels a day since 2004, down from 4 million in 2001 and 5.6 million in 2002. Although OPEC's excess capacity has rebounded from its 2005 low, the gains are largely in heavy crude oils that can only be processed in specialized refineries. These facilities are running at full capacity, so the added supplies are not relieving a tight market. The latest evidence also suggests OPEC is now restraining its output.



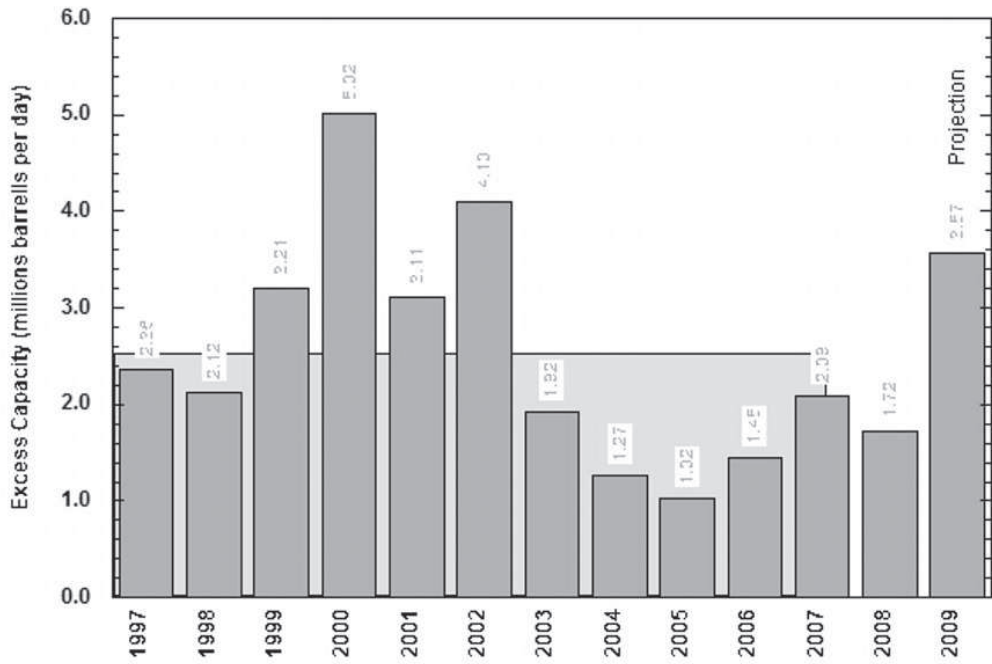


Fig. 8.1. Excess oil production capacity of OPEC and projection for 2009 (Adapted from [2]).

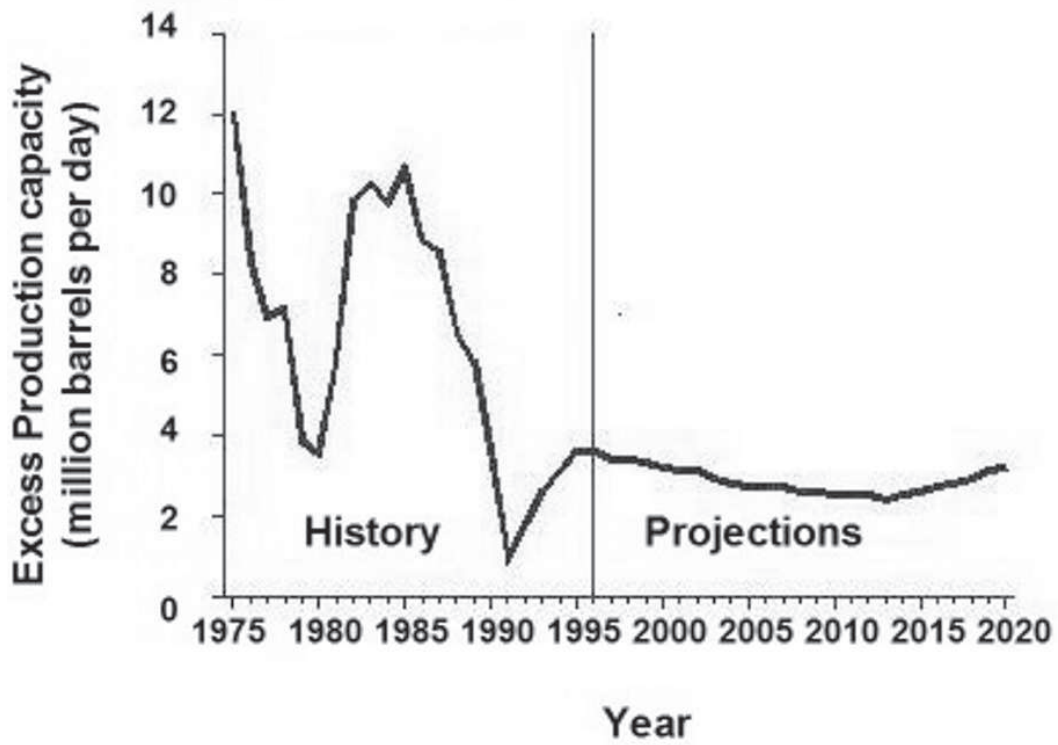


Fig. 8.2. The excess oil production capacity of the world (Adapted from [3]).

Forecasting world oil demand and production is becoming challenging. As shown in Fig. 8.3, among OPEC countries, basically all of the excess production capacity is with Saudi Arabia. The forecast, therefore, depends to a greater extent on the decision of Saudi Arabia's intent on production change.

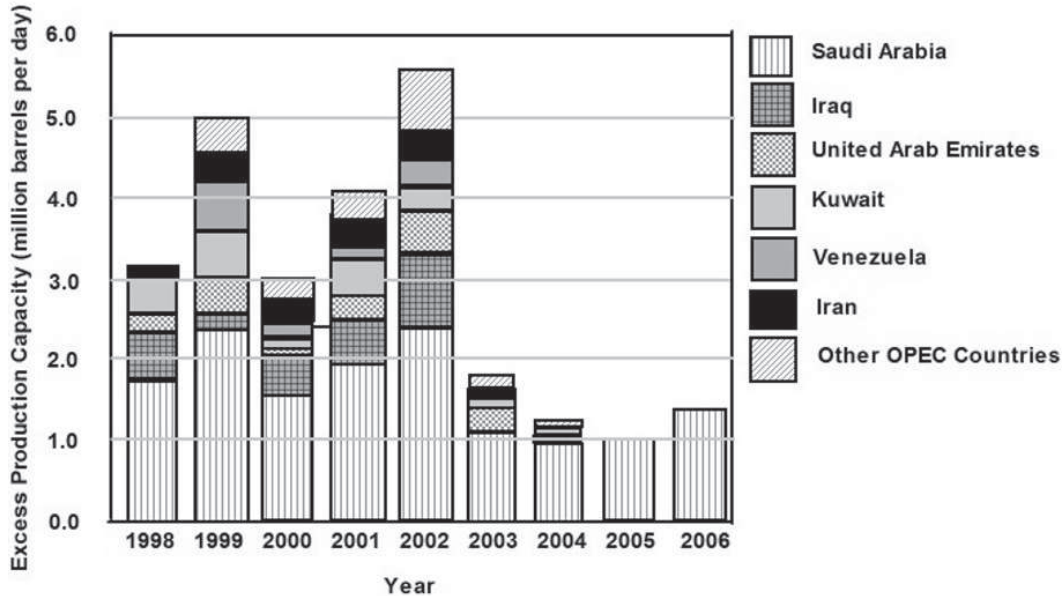


Fig. 8.3. Excess oil production capacities of OPEC countries (Adapted from [2]).

Recently (July 2, 2008), The U.S. Energy Information Administration has lowered its estimate for non-OPEC production in 2010 by 1.1 million barrels per day to 51.8 million barrels per day, from last year's forecast of 52.9 million. At the same time, the EIA lowered its 2010 OPEC production forecast by 400,000 barrels to 37.4 million.

However, it is reported by Associated Press (Abbot S, 07/04/2008) that Saudi Arabia's state-owned oil company, Aramco, is spending \$10 billion to build the infrastructure to pump 1.2 million barrels of oil per day by next June from the Khurais field and its two smaller neighbors. This will increase Saudi Arabia's total amount of oil production capacity to 12.5 million barrels per day by the end of 2009; up from a little more than 11 million barrels per day now.

The increased production may not be sufficient to bring down the price of crude oil. Although the consumption of oil is showing decline in the USA, it is increasing in other countries, particularly in China. The annual change in the consumption rate is shown in Fig. 8.4 and the actual consumption is shown in Fig. 8.5.

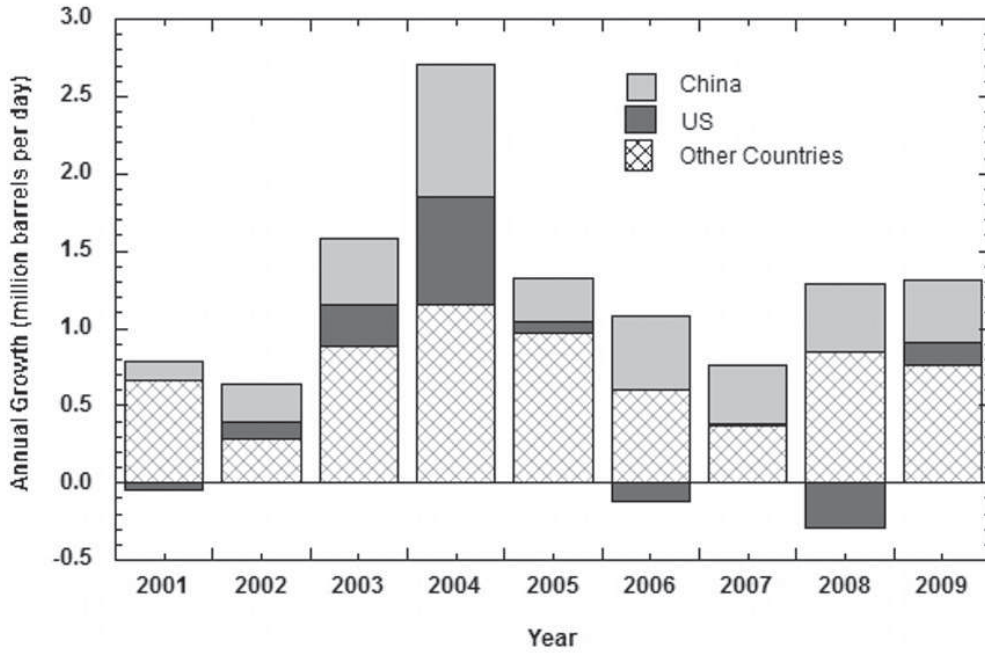


Fig. 8.4. Change in world oil consumption (Adapted from [4]).

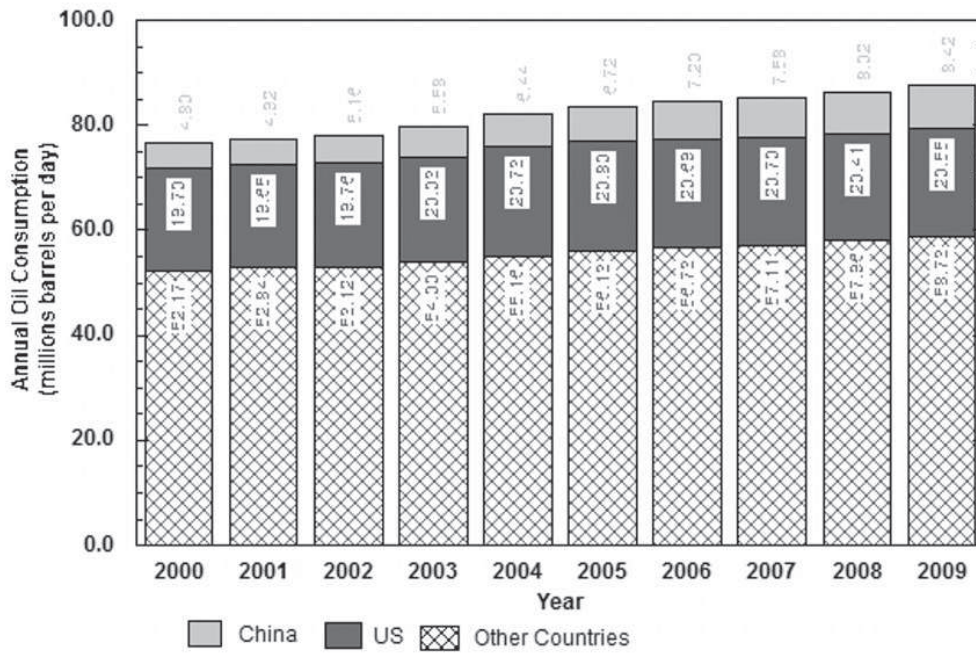


Fig. 8.5. Oil consumption by the USA and China, and rest of the world (Adapted from [4]).

The production of oil is not keeping up with the increasing demand. The world is increasingly becoming dependent on the supply from the OPEC countries. As can be seen from Fig. 8.6, although a number of non-OPEC countries including the USA have increased its production, at the same time the production capacity of a number of major oil producing countries is in a decline.

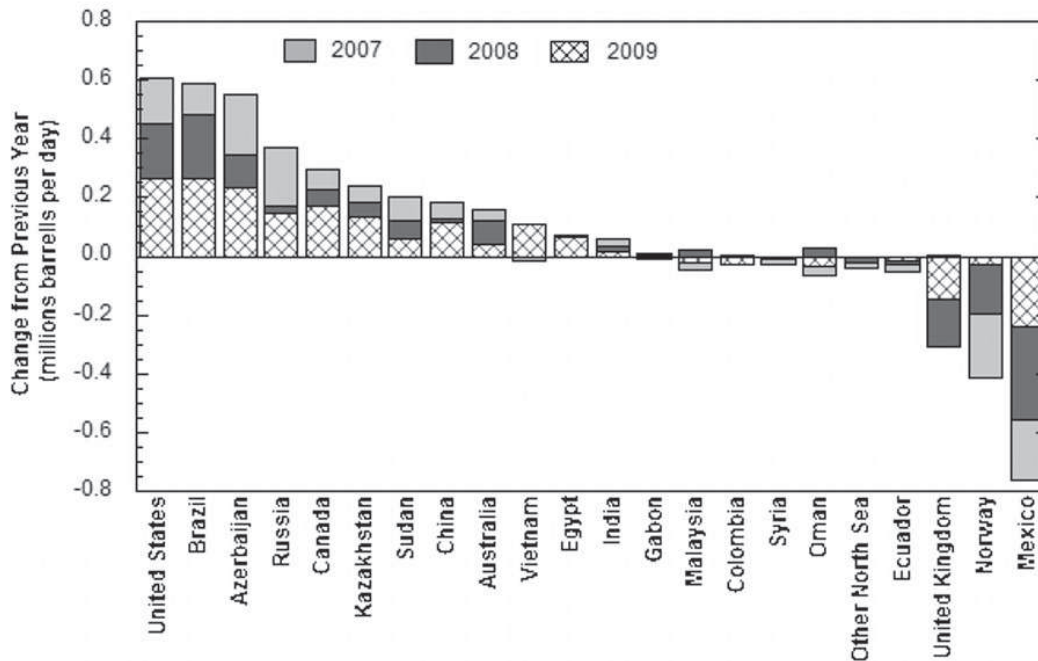


Fig. 8.6. Non-OPEC oil production growth; changes from the previous year (Adapted from [4]).

### 8.3 Oil Demand by Sectors

Most of the oil in the world is used by the transportation sector, which accounts for more than half of the total use. The industrial sector accounts for about 38% of the oil use, mostly for chemical and petrochemical processes. Consequently, much of the world's incremental oil demand is projected for use in the transportation sector (Fig. 8.7). Unconventional liquids such as gas-to-liquids, coal-to-liquids, ethanol and biodiesel produced from energy crops are expected to share some of the increased demand for transportation fuel; however, oil is still expected to be the major fuel of choice for transportation. An estimate of oil production by various oil producing countries in the future is given in Table 8.4.

In the USA, oil is mainly used for transportation accounting for about 70% of the total consumption. The uses of oil in various sectors in the USA are shown in Fig. 8.8.

**Table 8.4.** Forecast for future oil production by various oil producing countries.

Region /Country	Annual production				Annual growth		
	2006	2007	2008	2009	2007	2008	2009
OPEC Countries	35.823	35.410	37.096	37.082	-0.414	1.687	-0.014
North America	15.326	15.344	15.278	15.472	0.019	-0.066	0.194
Canada	3.288	3.356	3.416	3.585	0.068	0.060	0.169
Mexico	3.707	3.501	3.189	2.947	-0.206	-0.313	-0.242
United States	8.330	8.487	8.673	8.941	0.157	0.186	0.267
Russia and Caspian Sea	11.890	12.350	12.543	13.071	0.461	0.192	0.528
Russia	9.677	9.876	9.896	10.045	0.199	0.021	0.149
Azerbaijan	0.648	0.849	0.962	1.197	0.201	0.113	0.235
Kazakhstan	1.388	1.445	1.495	1.631	0.057	0.050	0.136
Turkmenistan	0.177	0.180	0.189	0.198	0.003	0.009	0.008
Latin America	4.560	4.597	4.799	5.013	0.037	0.203	0.213
Argentina	0.802	0.791	0.786	0.775	-0.012	-0.005	-0.011
Brazil	2.167	2.277	2.494	2.758	0.110	0.217	0.264
Colombia	0.544	0.543	0.545	0.518	-0.001	0.002	-0.027
Ecuador	0.537	0.512	0.497	0.482	-0.024	-0.015	-0.015
Other Latin America	0.509	0.473	0.477	0.480	-0.036	0.004	0.002
North Sea	4.780	4.544	4.191	4.019	-0.236	-0.352	-0.172
Norway	2.786	2.565	2.398	2.370	-0.221	-0.168	-0.027
United Kingdom	1.602	1.607	1.445	1.301	0.005	-0.162	-0.144
Other Non-OPEC	12.213	12.309	12.636	12.993	0.096	0.326	0.357
<b>World Total</b>	<b>84.591</b>	<b>84.554</b>	<b>86.543</b>	<b>87.650</b>	<b>-0.038</b>	<b>1.990</b>	<b>1.107</b>

Source: [BP Statistical Review of World Energy 2008, 2].

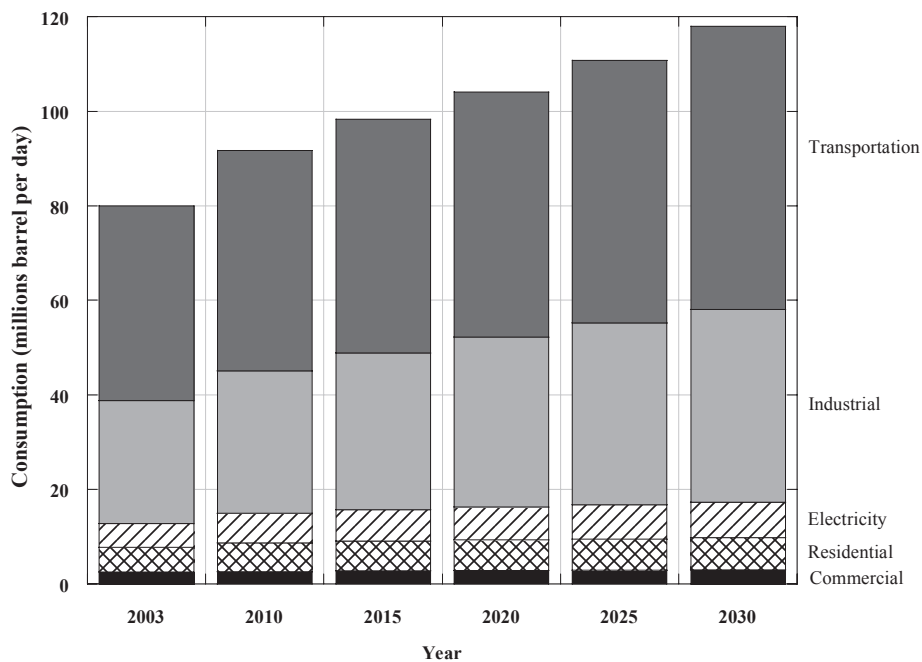


Fig. 8.7. World oil consumption by sectors (Adapted from [5]).

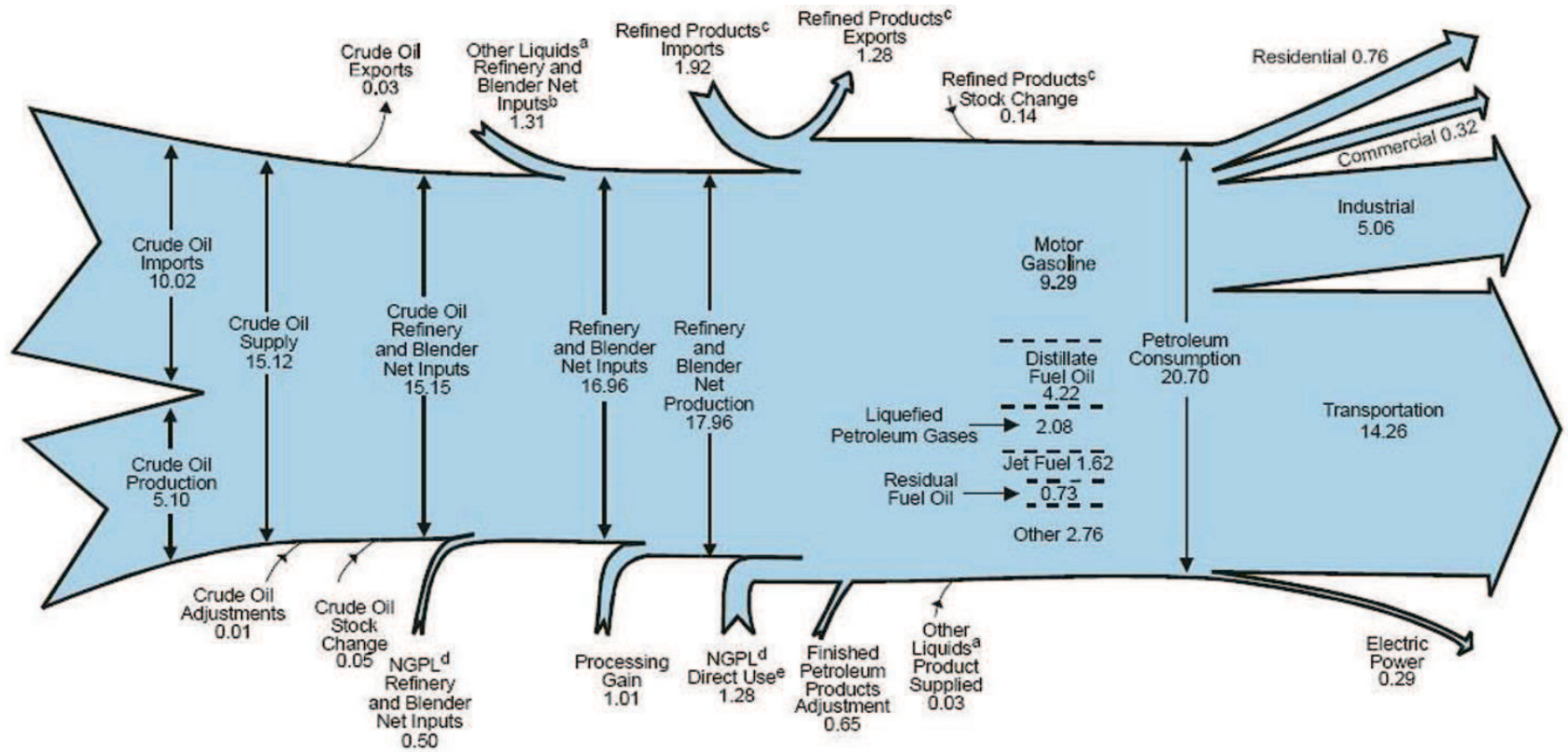
## 8.4 Exploration, Drilling, and Production

### 8.4.1 Exploration and Drilling

The search for oil and gas involved exploration both in land and off-shore, followed by drilling of exploratory wells. The methodologies for exploration and drilling techniques have been discussed in Chapter 7.

### 8.4.2 Production

The basic production steps and well completion are discussed in Chapter 7. The production techniques for oil only wells are discussed below. The naturally occurring pressure in the underground reservoir determines if the reservoir is economically viable. The pressure varies with the characteristics of the trap, the reservoir rock and the production history.



<sup>a</sup> Unfinished oils, other hydrocarbons/hydrogen, and motor gasoline and aviation gasoline blending components.

<sup>b</sup> Net imports (1.41) and adjustments (-0.05) minus stock change (0.02) and product supplied (0.03).

<sup>c</sup> Finished petroleum products, liquefied petroleum gases, and pentanes plus.

<sup>d</sup> Natural gas plant liquids.

<sup>e</sup> Production minus refinery input.

Notes: • Data are preliminary. • Values are derived from source data prior to rounding for publication. • Totals may not equal sum of components due to independent rounding.

Fig. 8.8. US petroleum flow 2007 (million barrels per day). <http://www.eia.doe.gov/emeu/aer/diagram2.html>.

For most oil wells, the pressure underground is high enough to force the oil to the surface. This is called *natural lift* production methods. Reservoirs in the Middle East tend to be long-lived on natural lift. As the underground pressure in the reservoir dissipates due to continuous extraction, the remaining oil is extracted by means of an *artificial lift*. A pump powered by gas or electricity is used for this purpose. The majority of the oil reservoirs in the United States are produced using some kind of artificial lift.

#### 8.4.2.1 Production by Artificial Lift

The artificial lift methods of producing oil from wells include (1) pumping with sucker rods (2) gas lift (3) hydraulic subsurface pumps (4) electrically driven centrifugal well pumps and (5) swabbing.

About 90% of the wells in the United States are equipped with sucker-rod-type pumps (see Fig. 8.9). This type of pumps is installed at the lower end of the tubing string and is actuated by a string of sucker rods extending from the surface to the subsurface pump [6]. The two common variations are mechanical and hydraulic long-stroke pumping. Other lifting mechanisms are jet pumps, and sonic pumps.



**Fig. 8.9.** Sucker rod type artificial lift pump for oil production (Printed with permission from [6]).

In the United States, primary production methods, including artificial lift, account for less than 40% of the total oil production. Once the primary production methods even with artificial lift become ineffective, the remaining oil is extracted



using “secondary” and/or “tertiary” production methods [7–35]. One common method for secondary production is called water flooding, in which the oil well is flooded using water to displace oil. Water forces the oil to the drilled shaft or “wellbore.” Finally, producers may need to turn to “tertiary” or “enhanced” oil recovery methods. These techniques are often centered on increasing the oil’s flow characteristics through the use of steam, carbon dioxide and other gases or chemicals. Secondary production methods account for about 50% and tertiary recovery is the remaining 10%.

The reservoir characteristics and the physical properties of the crude oil such as density and viscosity determine the cost of producing oil. These costs can range from \$2 per barrel in the Middle East to more than \$15 per barrel in some fields in the United States, including capital recovery. Technological advances in exploration, drilling, production methods have made it possible to produce oil cheaper in places such as deepwater Gulf of Mexico, where the production cost is about \$10 per barrel.

#### 8.4.2.2 Off-Shore Production

Significant advances have been made in the off-shore drilling and production techniques. In 1978, the greatest off-shore production depth was 300 m. In the 1990s, the crude oil production from the very deep offshore sectors provided stability to the global oil market. By 1998, the depth of the offshore production well was about 1,800 m at Petrobras in the Campos Basin in Brazil. Table 8.5 shows the advances in the deep offshore drilling and production of crude oil.

**Table 8.5.** Advances in the depth of production from the offshore basins.

<b>Oil field</b>	<b>Location</b>	<b>Year</b>	<b>Depth (m)</b>	
Cognac	Gulf of Mexico	1978	312	Shell Oil
Jolliet	Gulf of Mexico	1989	540	Conoco Inc.
Marlim	Campos Basin, Brazil	1991	752	Petrobras
Marlim 4	Campos Basin, Brazil	1994	1,027	Petrobras
Mensa	Gulf of Mexica	1997	1,650	Shell Oil
Marlim Sul	Campos Basin, Brazil	1997	1,709	Petrobras
Roncador	Campos Basin, Brazil	1999	1,852	Petrobras
Thusder Horse	Gulf of Mexico	2001	5,640 (ft)	BP and Exxon
Tupi	Brazil	2007	>3,000	Petrobras

For oil companies, the next target depth is 3,000 m. Meeting this objective constitutes a major industry challenge for the next 5–10 years.

## 8.5 Crude Oil Benchmarking

The physical and chemical properties of crude oils generally differ from one field to another field. These properties of the crude oils may even differ over the time from the same field. The quality of the crude oil, i.e., its physical and chemical consistency, is extremely important as it determines not only the crude oil processing (refining) techniques and re-processing necessary to achieve the optimal mix of product output, but also its market price. Price differentials between crude oils actually reflect the relative ease of refining. Based on the physical characteristics of the crude oils they are classified into different categories, which are called Crude Oil Benchmarking [36, 37]. Crude oils of similar quality are often compared to a single representative crude oil, a “benchmark,” of the quality class for pricing purposes worldwide. Crude oils are bought and sold in the stock markets as a commodity. The largest markets are in London, New York and Singapore, but crude oil and refined products – such as gasoline (petrol) and heating oil – are bought and sold all over the world.

Benchmarking of crude oils depends mainly on their density and sulfur content. Less dense (or “lighter”) crudes generally contain higher percentage of light hydrocarbons. The light hydrocarbons are most desired products as they are higher value products. Lighter crude can be separated (fractionated) by simple distillation process. The denser (“heavier”) crude oils require more extensive processing. The products from simple distillation are generally of lower value and require additional processing to produce the desired range of products.

Crude oil is considered “sweet” if it contains less than 0.5% sulfur. Sulfur is generally present as hydrogen sulfide. Small amounts of carbon dioxide may also be present in the crude. Light, sweet crudes are preferred by refiners because of their low sulfur content and relatively high yields of high-value products such as gasoline, diesel fuel, heating oil, and jet fuel. A higher sulfur content is undesirable for both processing and product quality.

Crude oil price Benchmarks were first introduced in the mid-1980s. There are three official benchmarks:

- West Texas Intermediate (WTI)
- Brent Blend
- Dubai Crude

Recently, two other benchmarking are used for trading and pricing purposes; New York Mercantile Exchange, and OPEC Basket.

### ***8.5.1 West Texas Intermediate (WTI)***

WTI is used primarily in the U.S. and is very light and very sweet. Its API (American Petroleum Institute) gravity is 39.6° (making it a “light” crude oil), and it contains only about 0.24% of sulfur (making it a “sweet” crude oil). This type of crude is suitable for producing low-sulfur gasoline and low-sulfur diesel. Although the production of WTI crude oil is on the decline, it still is the major benchmark of crude oil in the USA. WTI is generally priced at about a \$5 to \$6 per-barrel premium to the OPEC Basket price and about \$1 to \$2 per-barrel premium to Brent, although on a daily basis the pricing relationships between these can vary greatly.

### ***8.5.2 Brent Blend***

Brent blend is a mixture of crude oil from 15 different oil fields in the Brent and Ninian systems from the North Sea. Its API gravity is 38.3° (making it a “light” crude oil, but not quite as “light” as WTI), and sulfur content is about 0.37% making it a “sweet” crude oil, but slightly less “sweet” than WTI). Brent blend is ideal for making gasoline and middle distillates, both of which are consumed in large quantities in Northwest Europe, where Brent blend crude oil is typically refined.

Brent blend has become the de facto international oil benchmark. If no other information is given for a particular crude oil, its price is set in comparison to Brent Blend when traded at London’s International Petroleum Exchange (IPE) in the UK and other European markets. According to the IPE, Brent blend is used to price two thirds of the world’s internationally traded crude oil supplies. The physical value of North Sea Brent (“dated Brent”) is widely used in benchmarking the bulk of oil from the North Sea, West and North Africa, Russia and Central Asia, as well as large volumes from the Middle East heading into western markets.

The production of Brent blend, like WTI, is also on the decline, but it remains the major benchmark for other crude oils in Europe and Africa. Brent blend is generally priced at about a \$4 per-barrel premium to the OPEC Basket price or about a \$1 to \$2 per-barrel below WTI, although on a daily basis the pricing relationships can vary greatly.

### ***8.5.3 Dubai Crude***

In the Gulf, Dubai crude is used as a benchmark to price other regional crudes that are sold to Asia. Dubai crude is a medium heavy, low sulfur crude, typical of the

grades produced in the Persian Gulf. It is generally sold at a lower price than Brent blend and WTI.

### ***8.5.4 New York Mercantile Exchange***

Crude prices on the New York Mercantile Exchange generally refer to light, sweet crude. Oil containing more than 0.5% sulfur by weight is said to be “sour”. Not only the US domestic crude, but also a number of foreign crudes are traded based on this benchmarking.

The NYMEX miNY™ crude oil futures contract, designed for investment portfolios, is the equivalent of 500 barrels of crude, 50% of the size of a standard futures contract. The contract is available for trading on the CME Globex® (Chicago Mercantile Exchange) electronic trading platform and clears through the New York Mercantile Exchange clearinghouse.

The Exchange also lists for trading futures contract for Dubai crude oil; a futures contract on the differential between the light, sweet crude oil futures contract and Canadian Bow River crude at Hardisty, Alberta; and futures contracts on the differentials of the light, sweet crude oil futures contract and four domestic grades of crude oil: Light Louisiana Sweet, West Texas Intermediate-Midland, West Texas Sour, and Mars Blend.

### ***8.5.5 OPEC Basket***

The Organization of Petroleum Exporting Countries (OPEC) was founded in Baghdad, Iraq, in September 1960, mainly by oil producing countries from Middle East. The objective was to unify and coordinate members’ petroleum policies. Since 1982, OPEC also sets crude oil production quotas of its member countries. Current OPEC members include Iran, Iraq, Kuwait, Saudi Arabia, and Venezuela, Qatar, Indonesia, Libya, the United Arab Emirates, Algeria, and Nigeria. Although Iraq remains a member of OPEC, Iraqi production has not been a part of any OPEC quota agreements since March 1998.

OPEC collects pricing data on a “basket” of crude oils from its member countries. OPEC uses the price of this basket to monitor world oil market conditions. From January 1, 1987 to June 15, 2005, OPEC calculated an arithmetic average of seven crude oil streams, including: Algeria’s Saharan Blend, Indonesia Minas, Nigeria Bonny Light, Saudi Arabia Arab Light, Dubai Fateh, Venezuela Tia Juana and Mexico Isthmus (a non-OPEC oil) to estimate the OPEC basket price. This average is determined according to the production and exports of each country and is used as a reference point by OPEC to monitor worldwide oil market conditions.

From June 16, 2007, OPEC's reference basket consists of eleven crude streams representing the main export crude of all member countries, weighted according to production and exports to the main markets. The crude oil streams in the basket are:

1. Saharan Blend (Algeria)
2. Minas (Indonesia)
3. Iran Heavy (Islamic Republic of Iran)
4. Basra Light (Iraq)
5. Kuwait Export (Kuwait)
6. Es Sider (Libya)
7. Bonny Light (Nigeria)
8. Qatar Marine (Qatar)
9. Arab Light (Saudi Arabia)
10. Murban (UAE)
11. BCF 17 (Venezuela)

The API gravity for the new Basket is heavier, at 32.7° compared to 34.6° for the previous basket of seven crudes. The sulfur content of the new Reference Basket is 1.77%, making it more sour compared to the previous basket of 1.44%.

## 8.6 Crude Oil Characterization

A **crude oil assay** is the chemical evaluation of crude oil feedstock by various tests generally carried out in laboratories. Each crude oil type has unique chemical characteristics. No crude oil type is identical. Crude oil assays evaluate whole crude oils and various boiling range fractions of the crude oil. Assay data is used by refineries to determine if a crude oil feedstock is compatible for a particular petroleum refinery. The data also provide important information on the yield, quality, production rate, environmental problems, and marketing. An assay can be customized to meet specific requirements.

A crude oil assay involves a physical distillation of the crude oil to generate specific boiling range fractions ("cuts"). Each of the cuts is analyzed for physical and chemical properties, and basic or detailed information is provided regarding the whole crude properties and the individual cut qualities. The crude oil assay consists of the tests given in Table 8.6 along with the ASTM standards used for these tests. The detail characterization of a typical crude oil is given in Appendix VIII.

**Table 8.6.** Various test methods for characterization of petroleum.

Petroleum measurement	Unit	EN Test	IP Test	ISO Test	ASTM Test same	ASTM Test similar
Aromatics	% vol				nb. GC/MS	ASTM D5769
Aromatics	dm <sup>3</sup> /m <sup>3</sup>					
Aromatics	vol%		IP 156	ISO 3837	ASTM D1319	
Ash Content	%m/m	EN6245	IP 4	ISO6245	ASTM D482	
Benzene	dm <sup>3</sup> /m <sup>3</sup>	EN 12177	IP 425			ASTM D3606
Benzene	vol%					
Carbon Residue (Micro)	% m/m	EN10370	IP 398	ISO10370		ASTM D4530
Cetane number	None	EN5165	IP 41	ISO5165	ASTM D613	
Cetane Index	None	EN4264	IP 380	ISO4264	ASTM D4737	
CFPP	°C	EN116	IP 309			ASTM D6371
Cloud Point	°C	EN23015	IP 219	ISO3015		ASTM D2500
Copper corrosion	None	EN2160	IP 154	ISO 2160	ASTM D130	
Density at 15°C	kg/l	EN 3675	IP 160	ISO 3675	ASTM D1298	
Density at 15°C	kg/m <sup>3</sup>	EN 12185	IP 365	ISO 12185		ASTM D4052
Distillation (Rec. or Evap. Vol%)	°C	EN 3405	IP 123	ISO 3405		ASTM D86
Distillation, % Evap @ T°C	vol%					
Distillation, I.B.P	°C					
Distillation, F.B.P.	°C					
Distillation, Loss	vol%					
Distillation, Recovery	vol%					
Distillation, Residue	vol%					
Doctor test	None		IP 30			ASTM D4952
Existent gums	g/m <sup>3</sup>	EN 6246	IP 131	ISO6246	ASTM D381	
Existent gums	mg/100 mL		IP 131		ASTM D381	
Flash Point	°C	EN22719	IP404	ISO2719		D93
Induction period (Oxstab)	min.	EN7536	IP 40	ISO 7536	ASTM D525	
Kinematic Viscosity @ T°C	mm <sup>2</sup> /s	EN3104	IP 71	ISO3104	ASTM D445	
Lead	mg/L	EN 237	IP 428			ASTM D3237
Lubricity	um		IP 450	ISO12156		ASTM D6079

<b>Petroleum measurement</b>	<b>Unit</b>	<b>EN Test</b>	<b>IP Test</b>	<b>ISO Test</b>	<b>ASTM Test same</b>	<b>ASTM Test similar</b>
Mercaptans	mg/kg		IP 342	ISO 3012		ASTM D3227
Octane No. Motor	0	EN 25163	IP 236	ISO 5163	ASTM D2700	
Octane No. Research	0	EN 25164	IP 237	ISO 5164	ASTM D2699	
Olefins	vol%		IP 156	ISO 3837	ASTM D1319	
Olefins	dm <sup>3</sup> /m <sup>3</sup>					
Oxidation Stability	g/m <sup>3</sup>	EN12205	IP 388	ISO12205	ASTM D2274	
Oxygen	%m/m	EN 1601	IP 408		nb. GC OFID	ASTM D5599
Oxygenates	vol%					
Particulate Contamination	mg/kg	EN12662	IP 440			ASTM D6217
Polycyclic Aromatic Hydrocarbons	%m/m	EN12916	IP 391	ISO6591		
Sulfur	% mass or %m/m	EN8754	IP336	ISO8754		ASTM D4294
Sulfur	mg/kg	EN14596	IP 447	ISO14596		ASTM D2622
Sulfur	mg/kg		IP 490			ASTM D5453
Sulfur	mg/kg	EN 24260	IP 243	ISO4260	nb. Wickbold	
Vapor pressure. (RVP, ASVP, DVPE)	kPa	EN 13016	IP 394			ASTM D5191
Vapor pressure. (RVP, ASVP, DVPE)	hPa or mb		IP 69	ISO3007		ASTM D323
Vapor pressure. (RVP, ASVP, DVPE)	mmHg or torr					
Vapor pressure. (RVP, ASVP, DVPE)	kg/m <sup>2</sup>					
Vapor pressure. (RVP, ASVP, DVPE)	g/cm <sup>2</sup>					
Water Content	%m/m	EN 12937	IP 348	ISO 12937		ASTM D6304

## 8.7 Crude Oil Refining

Crude oil must be refined in order to produce finished products [38–49]. There are four basic operations that all the refineries perform for production of a variety of products. These are:

- Distillation
- Catalytic Reforming
- Cracking
- Treating

### 8.7.1 Distillation

The crude oil is heated and fed to a distillation column or tower. A number of such distillation columns are used in a refinery to produce a variety of products. The columns are operated at various temperatures and pressures. Depending on the operating pressure of the columns, they are called atmospheric column (Crude Distillation Unit) or vacuum distillation columns. During distillation, the lightest materials, such as propane and butane, vaporize and are collected from the top of the first atmospheric column. Medium weight materials, that include gasoline, jet and diesel fuels condense in the middle. Heavy materials, called gas oils, condense in the lower portion of the atmospheric column. The heaviest tar-like material, called residuum, is referred to as the “bottom of the barrel”, and is collected from the bottom of the column. Products from the top, middle and bottom of the column are transferred to different plants for further refining. A schematic diagram of a refinery for light oils is shown in Fig. 8.10.

The separation of the crude oil into various fractions depends on the temperature at a particular location of the column. Figure 8.11 shows the typical temperature at various locations of an atmospheric distillation column and the corresponding fractions.

The temperature at various locations of the column is maintained by using a variety of techniques. As can be seen from Fig. 8.12 a companion column is used along side the main crude distillation unit where a stream is drawn from the crude distillation column, heated, and again feed back to the crude distillation column. Also, a number of heaters are used to recover the waste heat and to pre-heat the crude oil.



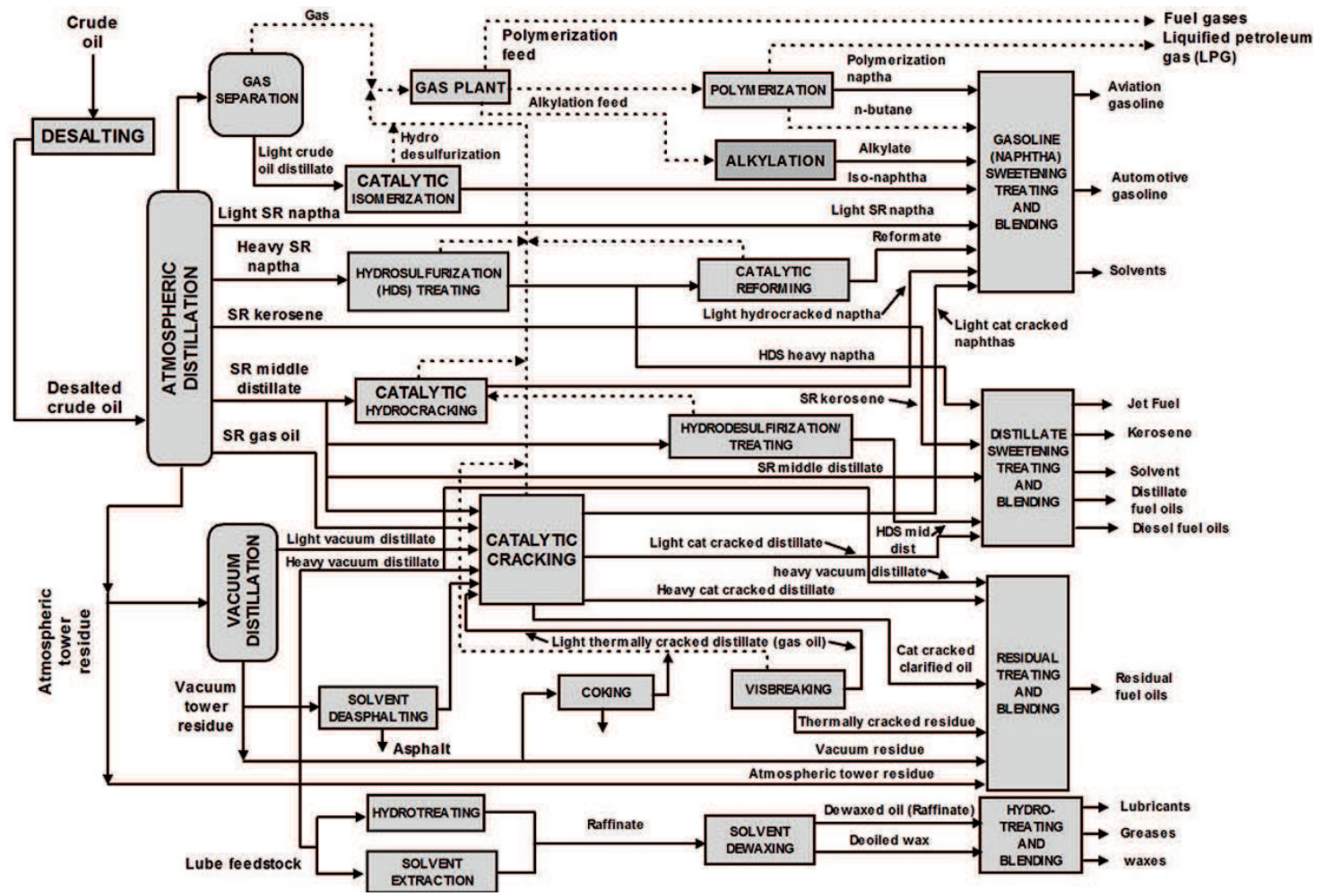


Fig. 8.10. Flow diagram of a crude oil processing refinery (Courtesy of [50]).

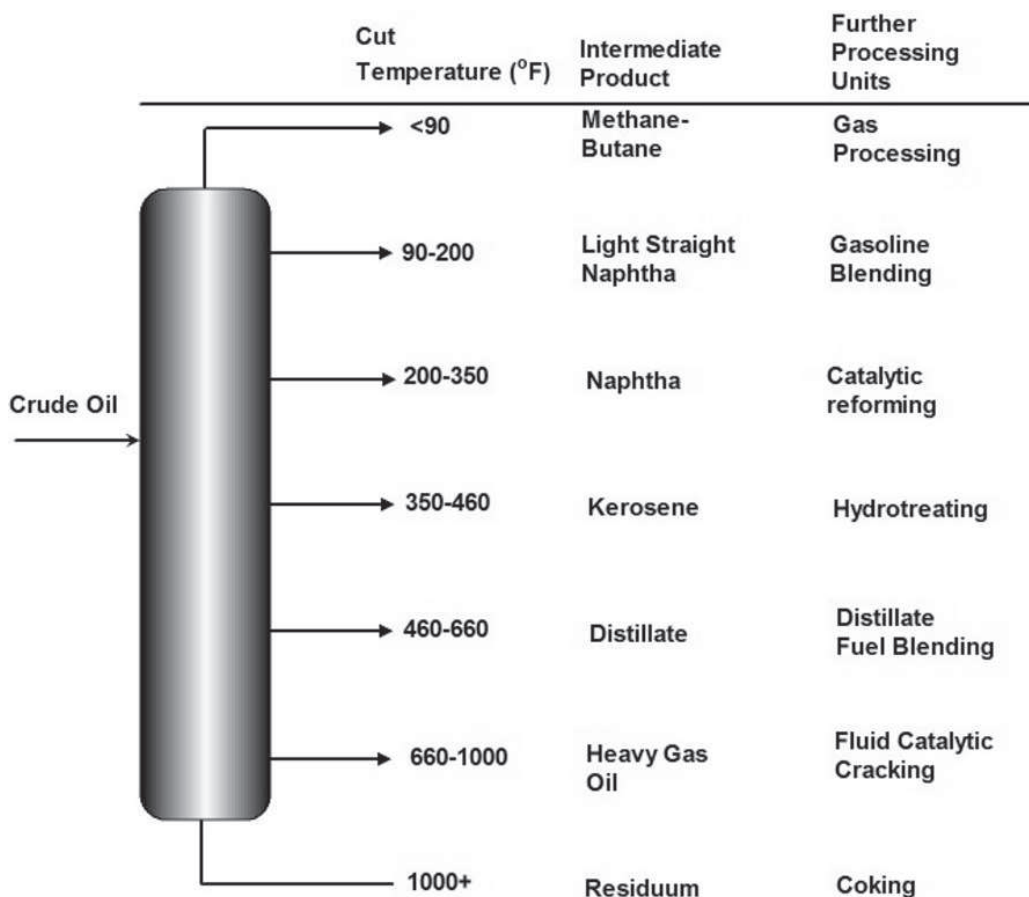


Fig. 8.11. Temperatures and corresponding fractions in the first step of crude oil distillation.

### 8.7.2 Catalytic Reforming

For use as a gasoline or motor fuel, the octane number of the finished product should be above 87. Catalytic reforming is one of the methods used for increasing the octane number of gasoline [51–60]. For motor fuel use, the octane number determines the quality of the product as it relates to the combustion characteristics of the fuel. A higher octane number reflects a lower tendency of the hydrocarbon to undergo a rapid, inefficient detonation in an internal combustion engine. The rapid detonation is undesirable as it causes knocking sound in the engine. In the USA, the octane number posted in the gas station is the arithmetic average of the MON (motor octane number which is measured at high engine speeds) and RON (research octane number which is measured at low engine speeds). The RON and MON of some selected hydrocarbons are given in Table 8.7. As can be seen from the table, aromatics have higher octane numbers and a greater percentage of them are desirable in the finished motor fuel products. The light petroleum distillates (naphtha) are catalytically reformed for the purpose of raising the octane number

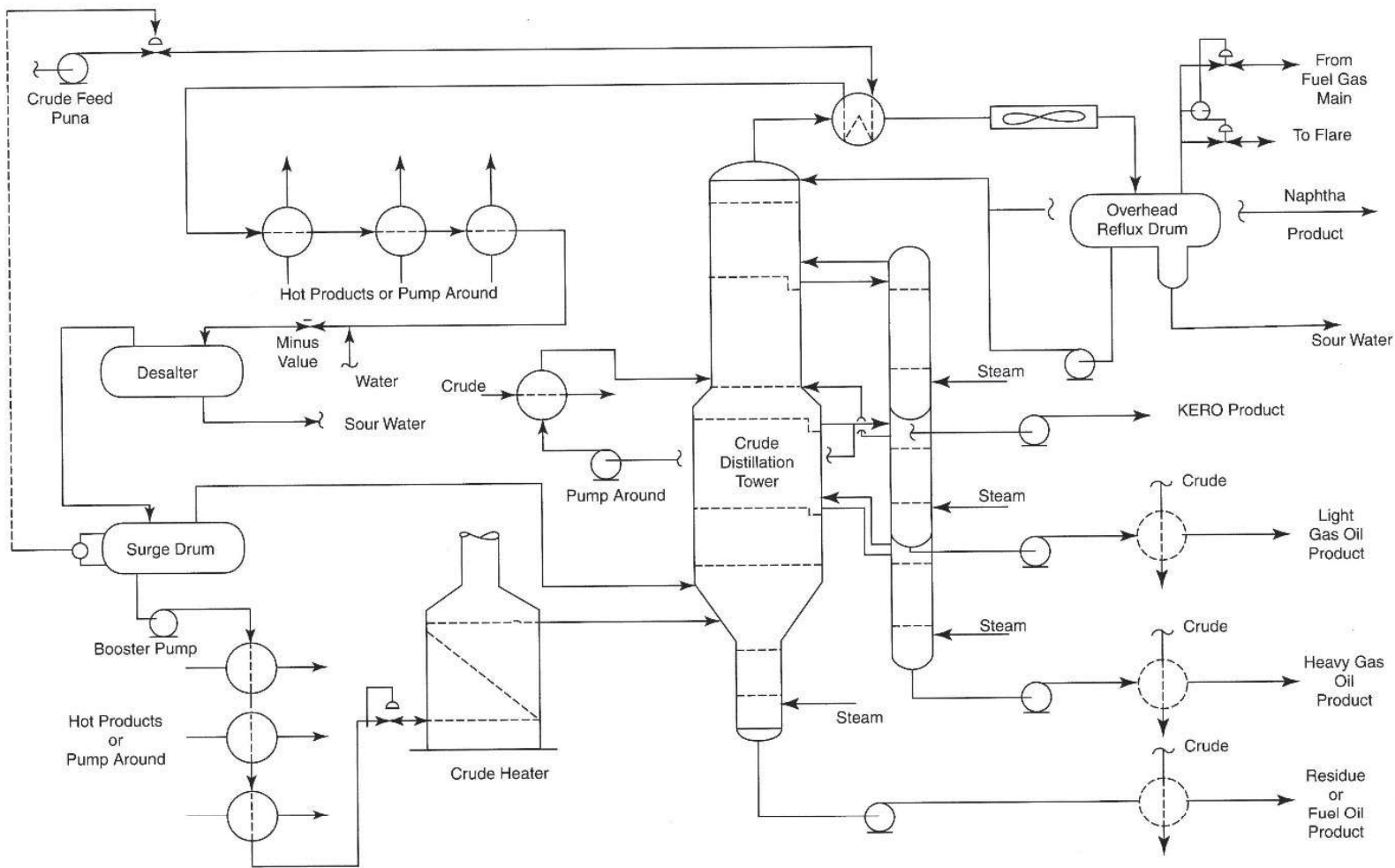


Fig. 8.12. The layout of a typical atmospheric crude oil distillation system (Printed with permission from [49]).

of the hydrocarbon feed stream. Naphtha is contacted with a platinum based catalyst at elevated temperatures (higher than 200°C (400°F)) and hydrogen pressures ranging from 345 to 3,450 kPa (50–500 psig). The low octane, paraffin-rich naphtha feed is converted to a high octane aromatic rich liquid product. The by-products of the process are hydrogen and light hydrocarbons. The UOP LLC first introduced the platinum based catalytic reforming unit (called Platforming™ process) in 1949. Since then significant improvement has been made, particularly in the catalyst area. The introduction of bimetallic catalysts allows lower pressure, higher severity operation: ~1,380–2,070 kPa (200–300 psig) at 95–98 octane number with typical cycle lengths of 1 year.

**Table 8.7.** Typical Research Octane Number (RON) and Motor Octane Number (MON) of some selected hydrocarbons.

Compounds	RON	MON
Paraffins		
n-Heptane	0	0
2-Methylhexane	42.4	46.3
3-Ethylpentane	65.0	69.3
2,4-Dimethylpentane	83.1	83.8
Aromatics		
Toluene	120.1	103.2
Ethylbenzene	107.4	97.9
Isopropylbenzene	113.0	99.3
1-Methyl-3-ethylbenzene	112.1	100.0
1,3,5-trimethylbenzene	>120	>120

Source: Reference [49]

Typical composition of the naphtha stream before and after the catalytic reforming is given in Table 8.8. The catalytically reformed naphthas are blend with various other streams to obtain the motor fuel with desired octane number.

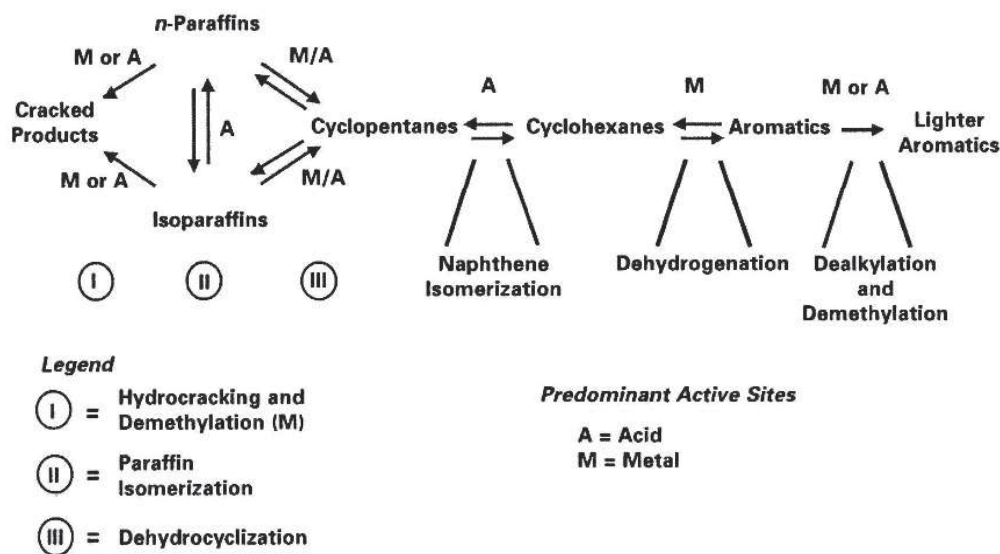
**Table 8.8.** Composition of a typical naphtha stream before and after catalytic reformation.

Compounds	Composition of Typical Naphtha (wt%)	Reformate Composition (wt%)
<b>Aromatics</b>		
Benzene	1.45	3.72
Toluene	4.06	13.97
Ethylbenzene	0.52	3.13
p-Xylene	0.92	3.39
m-Xylene	2.75	7.47
o-Xylene	0.87	4.83

<b>Compounds</b>	<b>Composition of Typical Naphtha (wt%)</b>	<b>Reformate Composition (wt%)</b>
C9+Aromatics	3.31	36.05
Total Aromatics	13.88	72.56
Total Olefins	0.11	0.82
<b>Paraffins and Napthenes</b>		
Propane	0.79	0.00
Isobutane	1.28	0.14
n-Butane	3.43	0.94
Isopentane	5.62	2.52
n-Pentane	6.19	1.74
Cyclopentane	0.64	0.10
C6 Isoparaffins	6.00	3.91
n-Hexane	5.3	1.74
Methylcyclopentane	2.58	0.28
Cyclohexane	3.26	0.03
C7-Isoparaffins	4.55	7.70
n-Heptane	4.65	2.22
C7 Cyclopentanes	2.77	0.33
Methylcyclohexane	7.57	0.04
C8 Isoparaffins	4.24	2.86
n-Octane	3.43	0.62
C8-Cyclopentanes	1.52	0.14
C8 Cyclohexanes	5.23	0.06
C9 Napthenes	3.63	0.04
C9-Paraffins	5.93	0.90
C10 Napthenes	1.66	0.04
C10-Paraffins	3.41	0.24
C11 Napthenes	1.04	0.00
C11-Paraffins	0.53	0.03
Total Paraffins	55.35	25.56
Total Napthenes	30.7	1.06

Source: Reference [49]

The objective of catalytic reforming is to produce lighter aromatics so that the octane number of the product stream increases. A number of reaction steps take place before the final products are obtained. The reaction steps are shown in Fig. 8.13 and the process flow diagram is shown in Fig. 8.14.



**Fig. 8.13.** Steps involved in catalytic reforming for production of light aromatics (Adapted from UOP, CCR platforming process for motor fuel production [61]).

Catalysts play an important role in the reforming process. Although platinum is the best catalyst, the cost of platinum makes the process very expensive. A number of non-platinum based catalysts have been developed. Also, zeolite was found to be an excellent support material for a number of active materials such as zinc [62–76]. Several modifications to the process have been made to improve its efficiency [77–81].

### 8.7.3 Cracking

The objective of the refinery is to maximize the production of transportation fuel; gasoline, jet fuel, and diesel. However, among these three, the greatest demand is for gasoline. The middle distillate, gas oil and residuum are converted into gasoline, jet and diesel fuels in a series of processing plants called cracking units, in which heavy hydrocarbon molecules break down into smaller, lighter ones. There are three applications of the cracking processes and are given in Table 8.9.

**Table 8.9.** Various objectives of catalyst cracking units.

Applications	Feedstock	Products
Gas oil cracking	Vacuum gas oils	Motor gasoline, LCO and LPG
Resid cracking	Atmospheric resid VGO and vacuum residues	Motor gasoline, LCO, and LPG
Cracking for petrochemicals	Vacuum gas oils and added residues	Light olefins-C <sub>2</sub> , C <sub>3</sub> , C <sub>4</sub> and aromatics

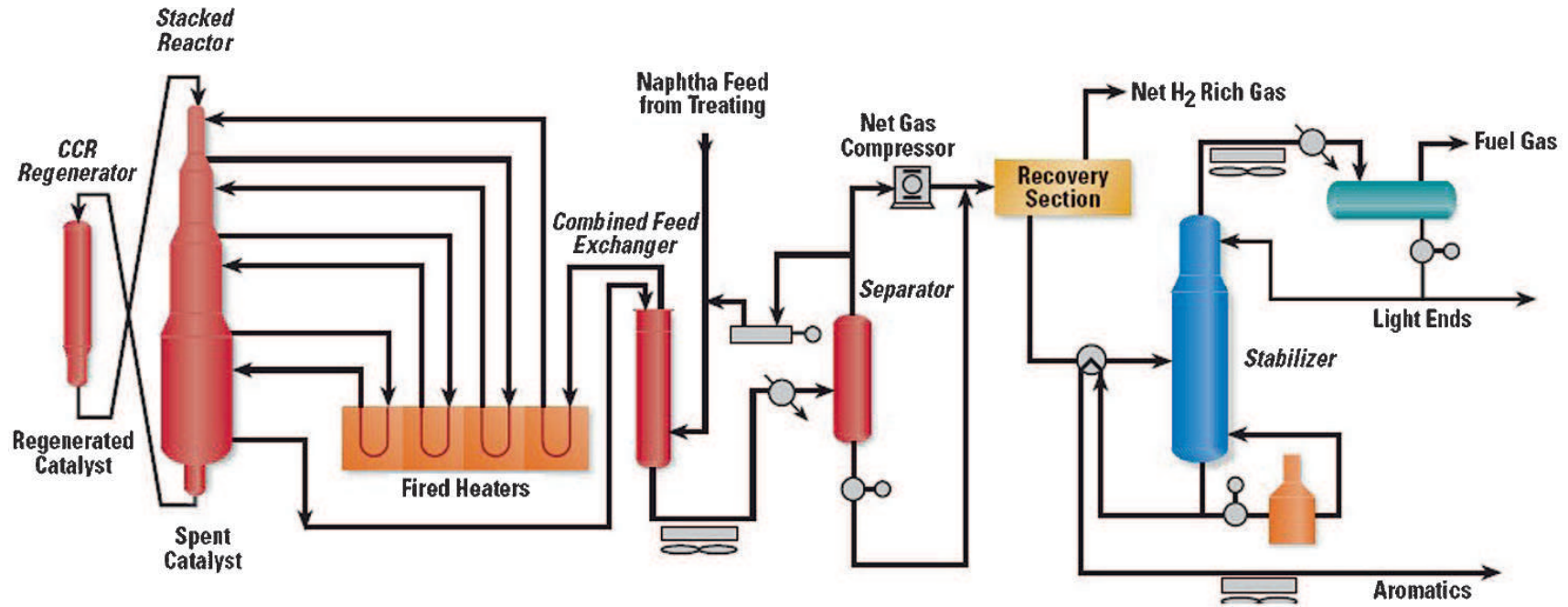


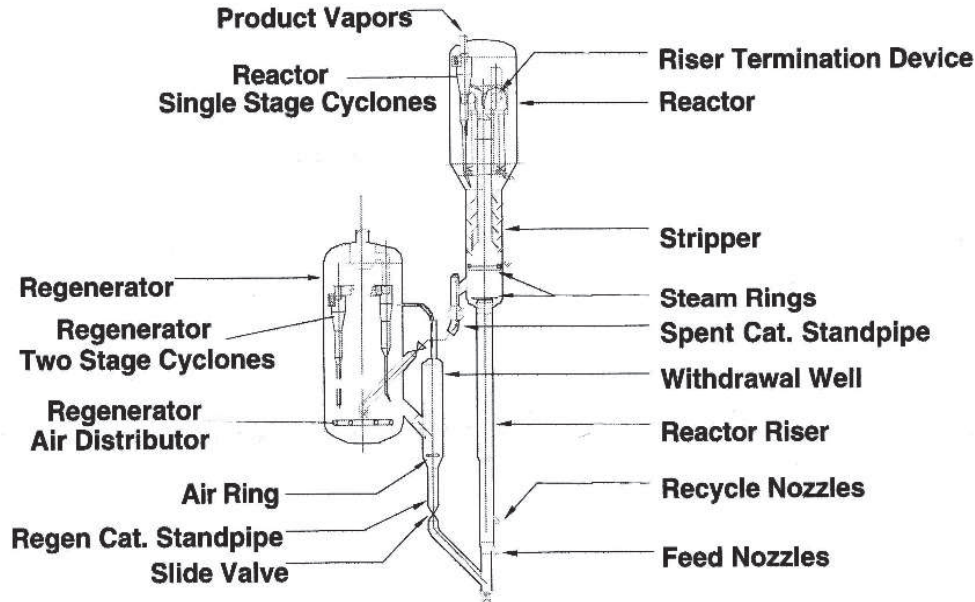
Fig. 8.14. Flow diagram of a catalytic reforming unit (Adapted from UOP, CCR platforming process for motor fuel production [61]).

Three basic cracking processes are used in the refinery to produce transportation fuels.

- Fluid Catalytic Cracking (FCC)
- Hydrocracking
- Coking (Thermal Cracking)

### 8.7.3.1 Fluid Catalytic Cracking (FCC)

In this process, heavy fractions of vacuum gas oil and resid (boiling point  $> 344^{\circ}\text{C}$  ( $650^{\circ}\text{F}$ )) are heated at  $1,000^{\circ}\text{F}$  under a vacuum in the presence of a catalyst to produce more valuable products such as Liquefied Petroleum Gas (LPG), gasoline, and diesel fuels [82–131]. A schematic diagram of a catalytic cracking unit (CCU) and a catalyst regeneration unit (CRU) is shown in Fig. 8.15. Catalysts contact the oil near the base of CCU riser where most of the reactions takes place. The reaction products and catalyst are separated in the catalyst/vapor separator. The vapor stream is further cleaned in a cyclone to remove any carried-over catalyst and fed to the main fractionators and the gas plant for separation of the products. The spent catalysts are regenerated by burning off the deposited coke from the catalyst surface and are fed back to the base riser of CCU. Typical CCU undergoes 100–400 such cycles a day.



**Fig. 8.15.** A typical fluid catalytic cracking unit. (From Letsch W (2006), Fluid catalytic cracking, Chapter 6, Handbook of Petroleum Processing, Eds. Jones DSJ, Pujado PR, Springer, 2006).



The chemical reactions that take place during cracking may be described by the following reactions. The basic reaction paths during fluid catalytic cracking are shown below. The process can be terminated at any point depending on the desired products.

*Gas Oil or Resid* → *Diesel* → *Gasoline* → *LPG + Coke*

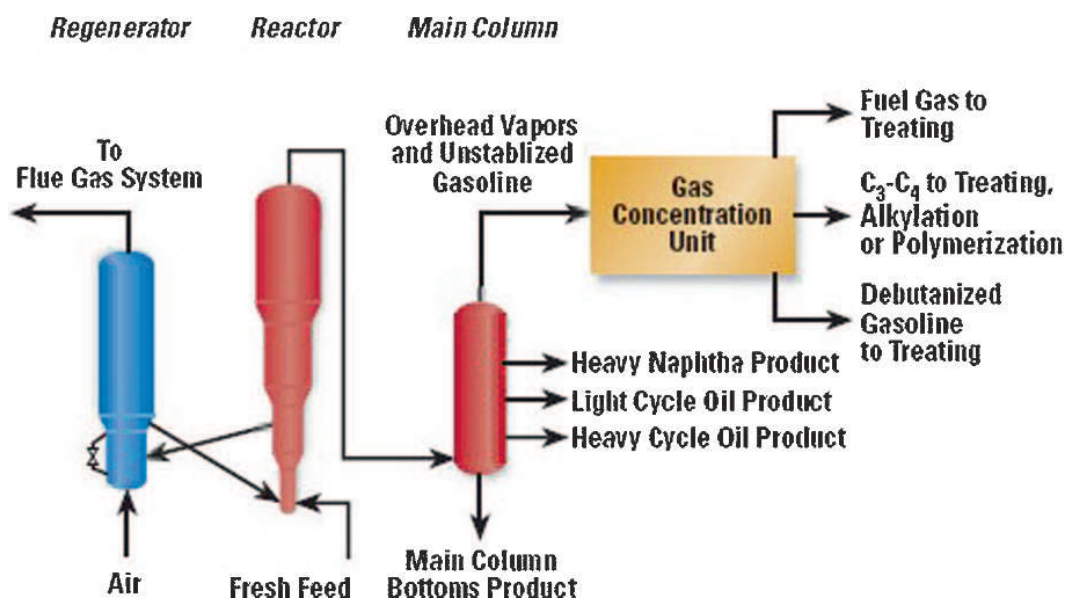
Paraffin → Paraffin + Olefin

$C_nH_{2n+2}$  →  $C_pH_{2p+2} + C_mH_{2m}$

$C_{10}H_{22}$  (Decane) →  $C_6H_{14}$  (Hexane) +  $C_4H_8$  (Butylene)

### 8.7.3.2 Gas Oil Catalytic Cracking

The design and operation of catalytic cracking unit for gas oil is shown in Fig. 8.16. A gas oil cracking unit consists of a feed injection system, reactor riser, riser termination system, and vapor quenching system. The feed, which is in the liquid form, is vaporized upon injection and is contacted with the catalyst. The regenerated and recycled catalyst from the catalyst regenerator is hot; the feed injection system should cool it down as quickly as possible before its contact with the feed. The other feature of the injection system is that it should provide plug flow of the feed. Various feed injection systems, reactor with riser and quench system, and catalyst regenerators are developed to improve the efficiency of the system.



**Fig. 8.16.** A gas oil cracking unit (From UOP Fluid catalytic cracking unit (FCC) and related processes, UOP [61]).

### 8.7.3.3 Resid Catalytic Cracking

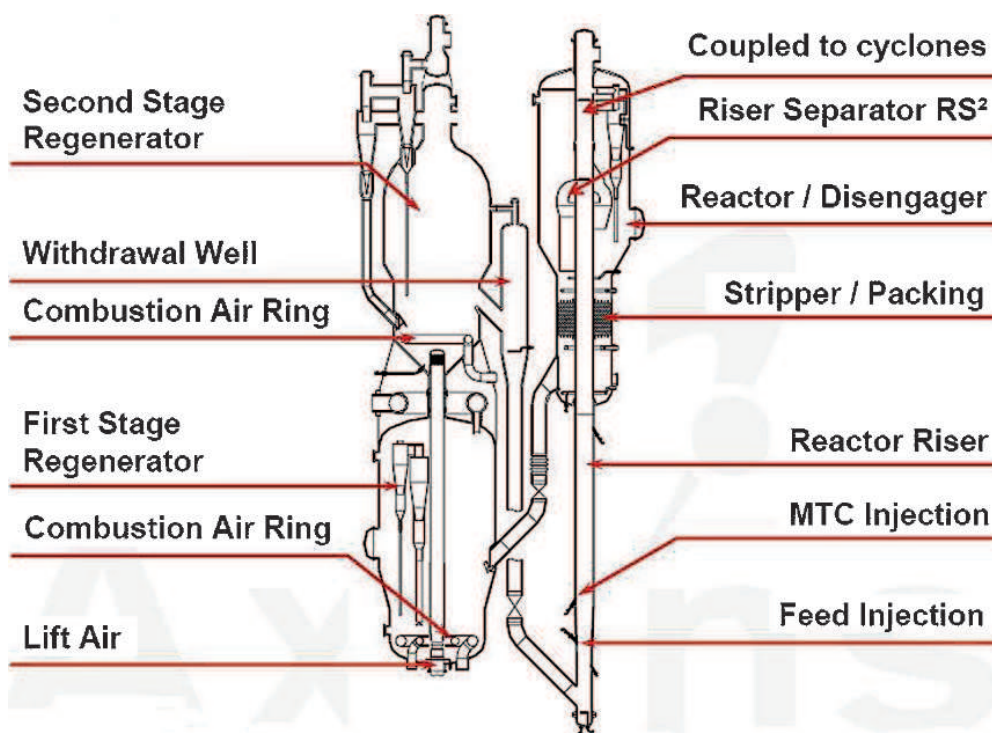
Refineries are under increasing pressure to process high boiling point feeds and crude oils with high levels of contaminant metals. Residue catalytic cracking process was developed to further process high boiling residue. One of the main issues was development of catalysts. A catalyst should have the following characteristics in order to be effective and economical.

- Capability to passivity contaminant metals such as nickel and vanadium
- Capable of cracking higher boiling range molecules
- A high activity and stability

The catalyst generally used for resid cracking is elite Type Y because of its high hydro-thermal stability, up to a temperature of 1,600°F, three-dimensional structure, average pore diameter of 7.5 Å, high activity and selectivity. Elite Type Y resid catalysts offer low production of coke and preservation of elite integrity and activity, and inertness in the presence of high concentrations of nickel and vanadium. A number of companies produce catalysts for RFCC (Resid Fluid Catalytic Cracking) units with varying composition and characteristics.

Although the basic design is the same, resid catalytic cracking units differ based on a specific task that needs to be carried out. The feed injection system should be capable of handling heavier feed which requires more steam for proper dispersion of the feed into the reactor. The main difference of a RFCC with other FCC is in the design of the regenerator. The regenerator should be designed such a way that the regenerated catalyst is cooled down before recycling back to the cracking unit. Either a single stage regenerator with a catalyst cooler or a two-stage regenerator is used. Currently most of the RFCC units employ two-stage regenerator. It not only cools down the catalyst, but a two-stage regenerator produces CO rather than CO<sub>2</sub>. This can reduce or even eliminate the need for any heat removal system. Another advantage is that most of the hydrogen (about 80–85% of initial hydrogen content) in the coke can be burnt off in the first stage of the regenerator leaving no carbon on the catalyst surface. The moisture produced during combustion of hydrogen tends to deactivate the catalyst. Therefore, catalysts should be hydro-thermally stable. A typical resid cracker is shown in Fig. 8.17.

Fluid catalytic cracking is one of the main processes for upgrading the product quality and yield. Significant efforts have been directed towards research and process development [82–96]. The catalysts used in the FCC units play a major role. A number of researchers focused their attention on development of new catalysts or modification of existing catalysts [97–112]. Among various catalysts, ZSM based catalysts are explored heavily recently due to its high temperature stability and capability to retain activity [113–118]. One of issues with the FCC process is the regeneration of catalysts for repeated use [119–124]. This will not only extend the life time of the catalyst, but also reduce the operating costs. The riser design of FCC units is important for product quality and yield [125–131].



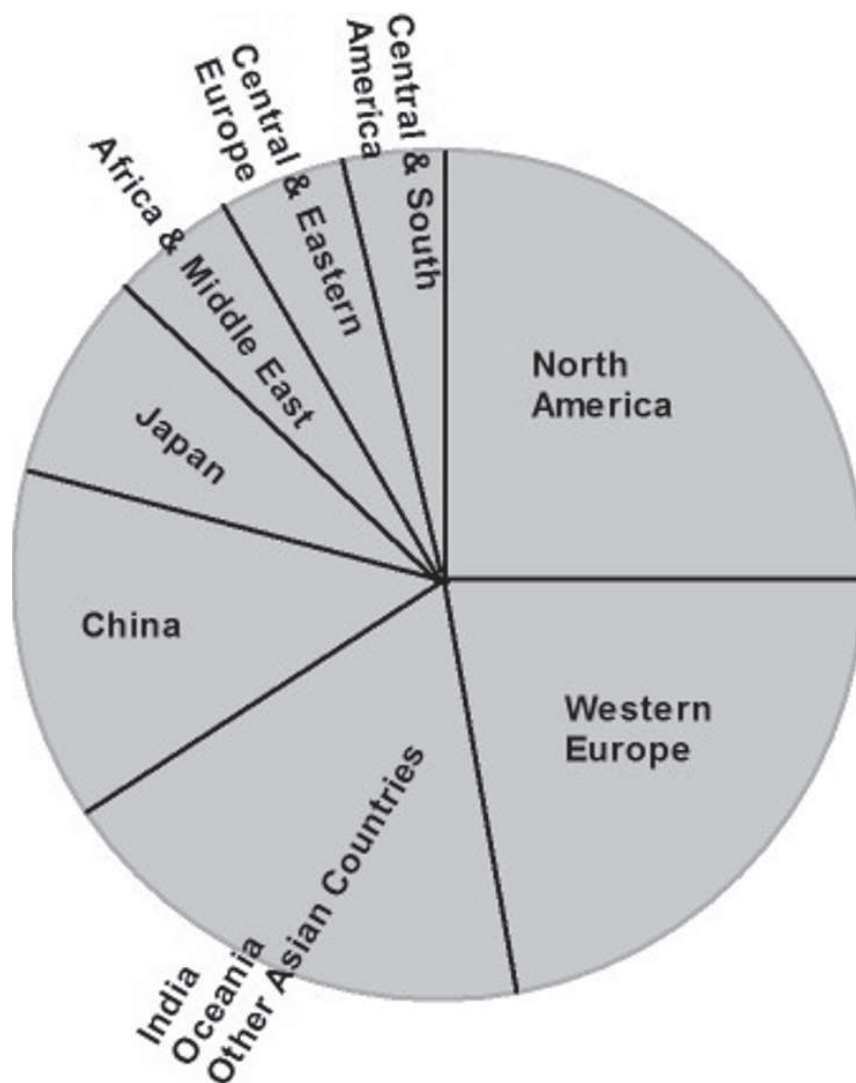
**Fig. 8.17.** A resid catalytic cracking unit developed by Axens IFP group (From Roux R (2004) A new separator helps FCC adapt to a new refinery-petrochemical role. Axens IFP Group Technologies, PETEM 2004).

## 8.8 Cracking for Light Olefins and Aromatics

One of the main objectives of cracking heavier feedstock is to produce light olefins, mainly propylene. The demand for propylene as a petrochemical feedstock has increased significantly in recent years.

In 2006, worldwide production of propylene for chemical uses amounted to almost 70,000 metric tons and was valued at roughly \$80 billion. Consumption of propylene worldwide is expected to grow at an average annual rate of about 5% over the 5-year period from 2006 to 2011.

The major use of propylene is in the production of polypropylene; almost 61% of the world's propylene was used for polypropylene production in 2006. In Fig. 8.18 the major consumers of propylene are shown. Other uses of propylene include production of acrylonitrile, oxo chemicals, propylene oxide, cumene, isopropyl alcohol and polygas chemicals. Since propylene is an established market, no significant new chemical uses are expected to emerge in the future.



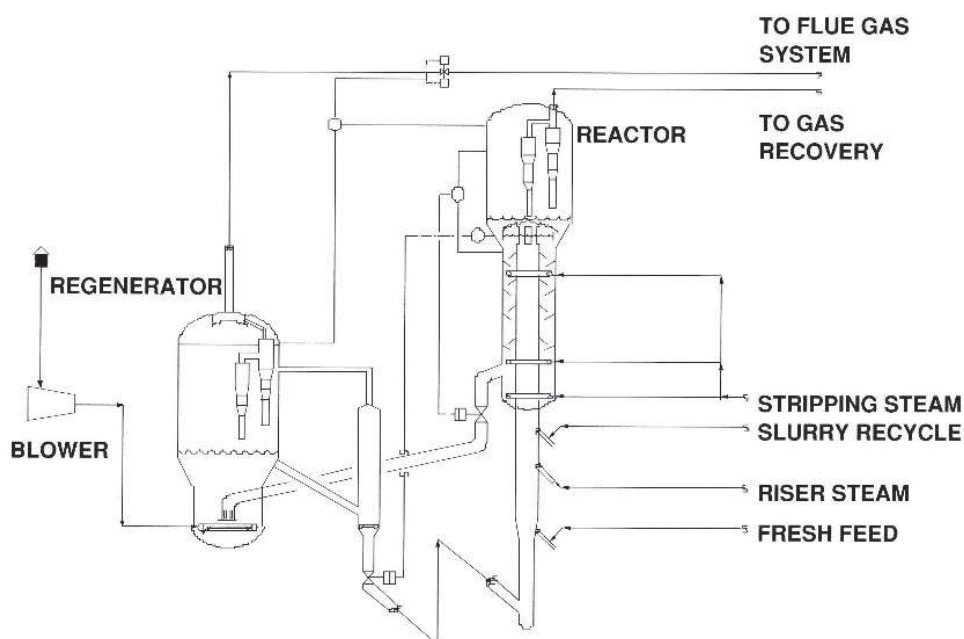
**Fig. 8.18.** Consumption of propylene in various regions of the world and by some selected countries.

Three major cracking processes; Deep Catalytic Cracking (DCC), Fluid Catalytic Cracking (FCC), and Steam Cracking (SC) are currently used for production of propylene [134–141]. Various products yield by these processes is given in Table 8.10. Although the total product yield by SC is higher than DCC or FCC, the combined aromatic and olefin fractions is higher for DCC process. A schematic diagram of DCC process is shown in Fig. 8.19. The basic operation is the same as that of a gas-oil cracking unit. A number of feedstock can be used in DCC units including vacuum gas oil (VGO), hydrotreated VGO, coker gas oil, and atmospheric resid. Two processes have been developed recently; PetroFCC by UOP and Maxofin by Kellogg Brown & Root-Halliburton to increase the propylene yield from heavy feeds.

**Table 8.10.** Yield of products by three cracking processes.

Components	DCC	FCC	SC
Paraffins	14.3	28.6	3.5
Olefins	32.4	35.3	13.3
Naphthenes	5.0	9.8	4.1
Aromatics	48.3	26.3	79.1
<b>Aromatics Breakdown</b>			
Benzene	1.9	0.6	37.1
Toluene	9.4	2.4	18.9
C <sub>8</sub>	15.6	6.7	13.5
C <sub>9</sub>	12.1	12.5	5.4
C <sub>10</sub> <sup>+</sup>	9.3	4.1	4.2
Total	48.3	26.3	79.1

Source: Reference [49].



**Fig. 8.19.** Schematic diagram of a deep catalytic cracking unit (From W. Letzsch, Fluid catalytic cracking, Chapter 6, Handbook of Petroleum Processing, Eds. DSJ Jones and PR Pujado, Springer, 2006 [132]).

The PetroFCC process flow diagram is shown in Fig. 8.20 and the cracking unit is shown in Fig. 8.21. Most of the technologies employed in PetroFCC are adopted from their UOP-FCC units. The spent catalyst is recycled back to the feed riser following regeneration. Interestingly, according to UOP, the spent catalyst is less active, but more selective than the clean regenerated catalyst. The operational conditions of PetroFCC for enhanced olefin productions are; hydrocarbon pressure: 10–30 psia, temperature: 1,000–1,150°F, and shape selective additives: 10–25 wt% of catalyst. The yield of various olefins from PetroFCC is compared with FCC in Table 8.11.

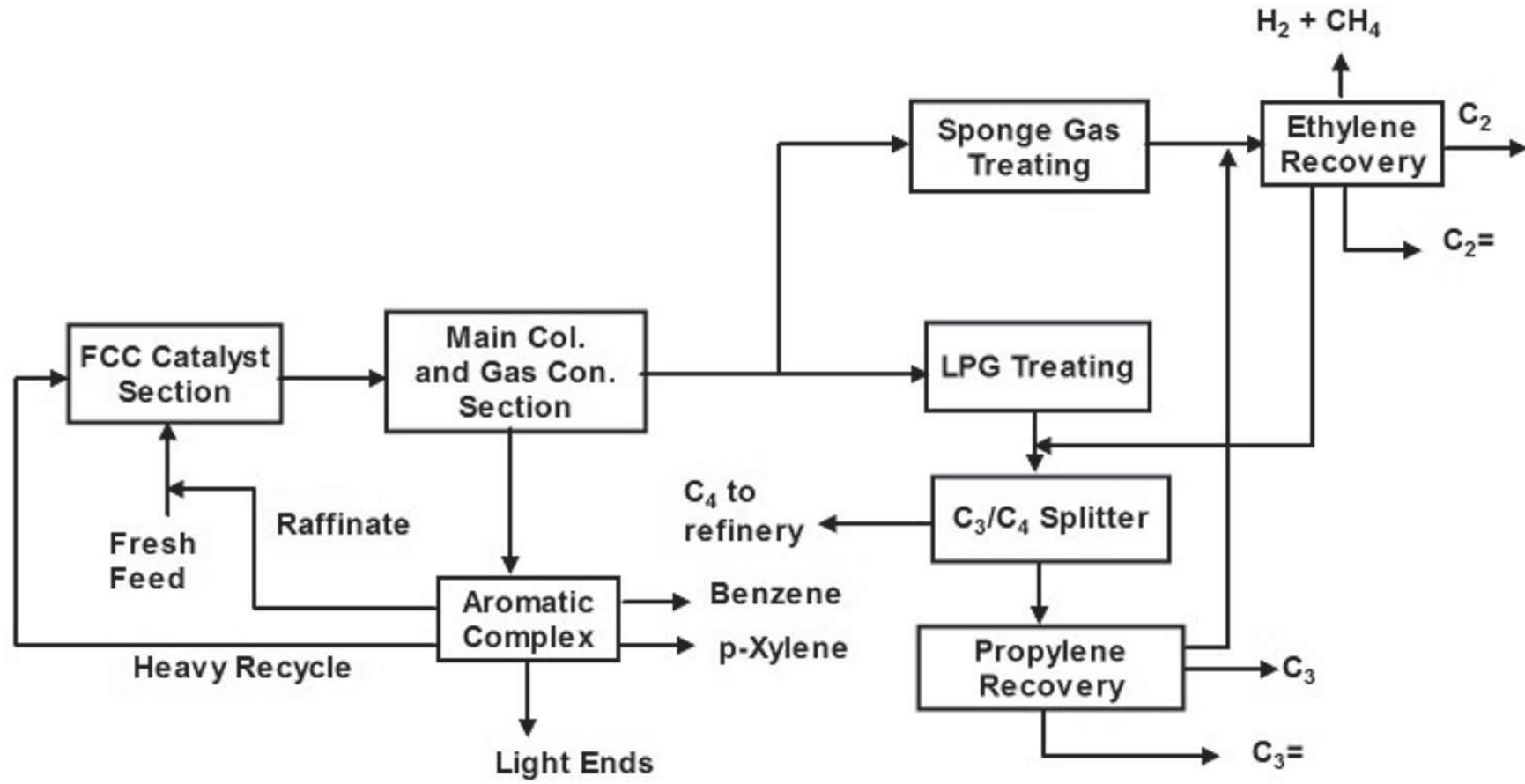
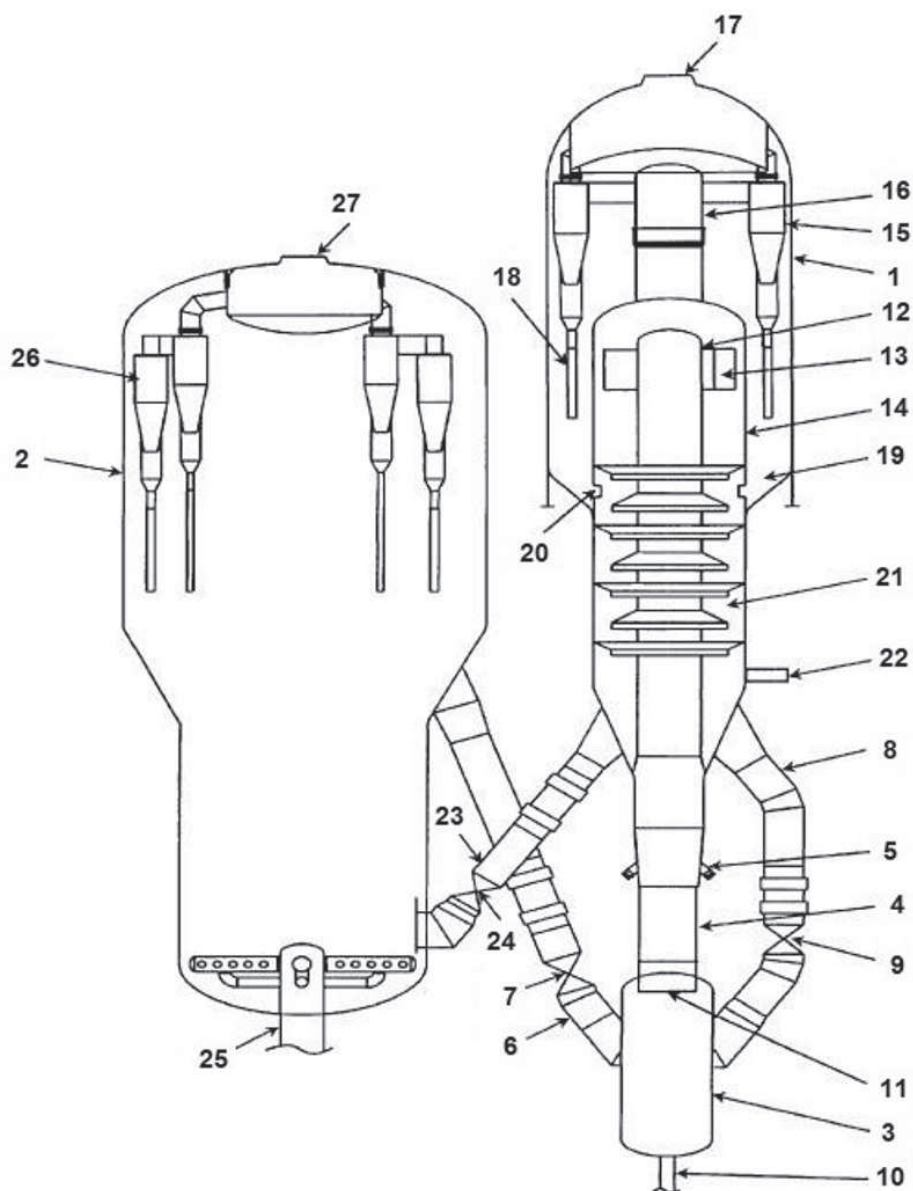


Fig. 8.20. The process flow diagram of a PetroFCC unit.



1	Separator vessel	15	Cyclone
2	Regenerator	16	Conduit
3	Blending vessel	17	Outlet
4	Vertical riser	18	Dipleg conduit
5	Nozzle	19	Catalyst Bed
6	Regenerator sandpipe	20	Opening to stripping zone
7	Control valve	21	Stripping zone
8	Recycle conduit	22	Line
9	Control valve	23	Coked catalyst conduit
10	Conduit	24	Control valve
11	Inlet to riser	25	Inlet
12	Swirl arm arrangement	26	Cyclone
13	Outlet	27	Vessel outlet
14	Chamber		

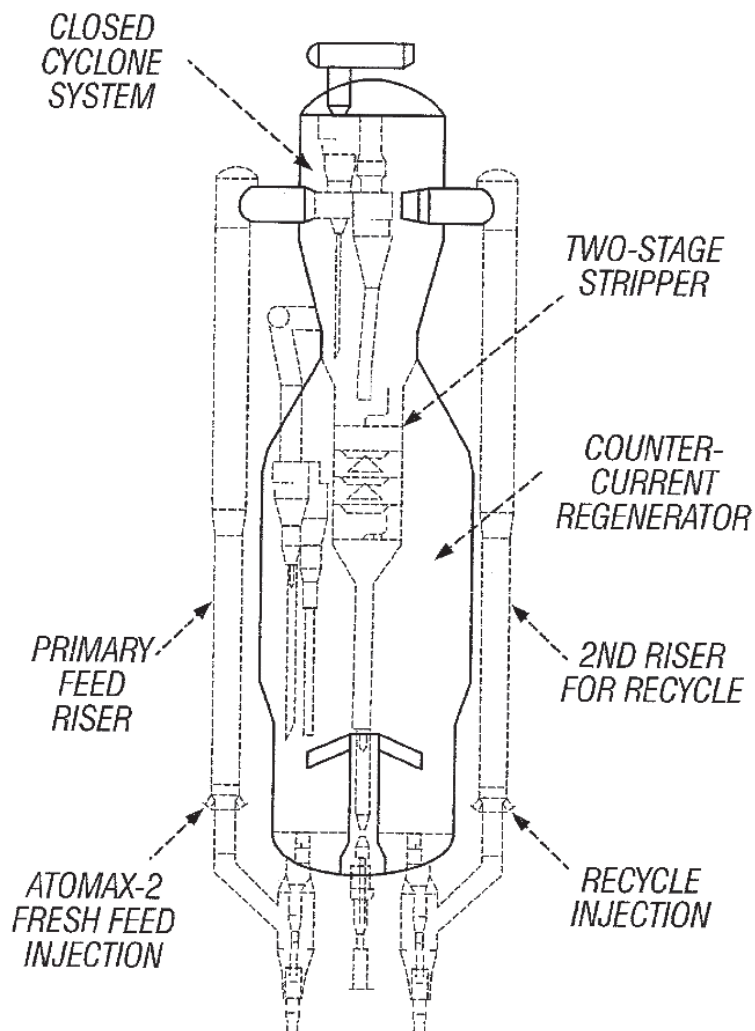
**Fig. 8.21.** Cracking unit assembly for PetroFCC unit.

**Table 8.11.** Comparison of yields of various olefins between PetroFCC and FCC processes.

Compounds	PetroFCC	FCC
Propylene	22	4.7
Butylene	14	~6
Ethylene	6	~1
Gasoline	28	53.5

Source: Reference [49].

Maxofin process is designed to maximize propylene production. The main reactor is shown in Fig. 8.22. It has a stacked reactor-regenerator configuration. A special ZSM-5 additive is used along with the FCC catalyst to enhanced propylene selectivity. The yield from the Maxofin process for a gas oil feed operating at three different modes is given in Table 8.12.



**Fig. 8.22.** The main reactor of the Maxofin process. (From Tallman MJ, Santner C, Miller RB (2006) Integrated catalytic cracking and steam pyrolysis process for olefins- US Patent 7,128,827 [142]).



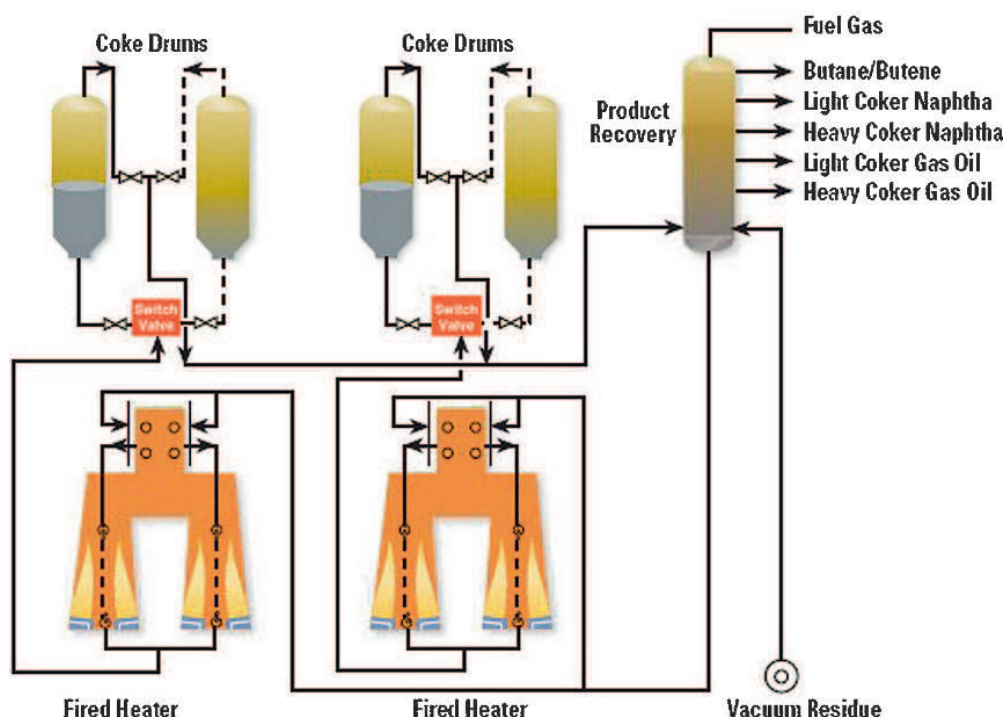
**Table 8.12.** Yields from Maxofin unit.

	Max C <sub>3</sub> =	Intermediate	Max Fuels
Recycle	Yes	No	No
ZSM-5	Yes	Yes	No
Riser Temp, oC	538/593	538	538
Yields (wt%)			
C <sub>2</sub> Minus	7.6	2.3	2.2
Ethylene	4.3	2.0	0.9
Propylene	18.4	14.4	6.2
Butylene	12.9	12.3	7.3
Gasoline	18.8	35.5	49.8
Coke	8.3	6.4	5.9
Conversion	86.4	87.7	85.4

Source: Reference [49].

## 8.9 Delayed Coking Unit (Coker)

In a Delayed Coking Unit (Coker), low-value residuum is converted to high-value light products, producing petroleum coke as a by-product by using mainly heat [143–150]. The large residuum molecules are cracked into smaller molecules when the residuum is held in a coke drum at a high temperature for a period of time. Only solid coke remains and must be drilled out from the coke drums. A schematic diagram of the Coker from the UOP is shown in Fig. 8.23.



**Fig. 8.23.** A delayed coking unit developed by UOP.

## 8.10 Hydrocracking

Hydrocracking utilizes hydrogen gas and a catalyst to modify the residue feed stream into various products [151–172]. Only carbon–carbon bonds are broken and hydrogen immediately saturates any olefins that are formed. Hydrocracking can produce LPG, naphtha, kerosene and distillates and a range of products depending on the type of feed to the unit.

It proceeds by two main reactions: hydrogenation of higher unsaturated hydrocarbons followed by cracking them to the required fuels. The process is carried out by passing oil feed together with hydrogen at high pressure (1,000–2,500 psig, or 7–17 MPa) and moderate temperatures (500–750°F or 260–400°C) into a reactor with a bifunctional catalyst, comprising an acidic solid and a hydrogenating metal component. Gasoline of high octane number is produced, both directly and through a subsequent step such as catalytic reforming; jet fuels may also be manufactured simply by changing conditions with the same catalysts.

Generally, the process is used as an adjunct to catalytic cracking. Oils, which are difficult to convert in the catalytic process because they are highly aromatic and cause rapid catalyst decline, can be easily handled by hydrocracking process. The low cracking temperature and the high hydrogen pressure, which decreases catalyst fouling, make the process more favorable. The most important components in any feed are the nitrogen-containing compounds, since these are severe poisons for hydrocracking catalysts and must be almost completely removed.

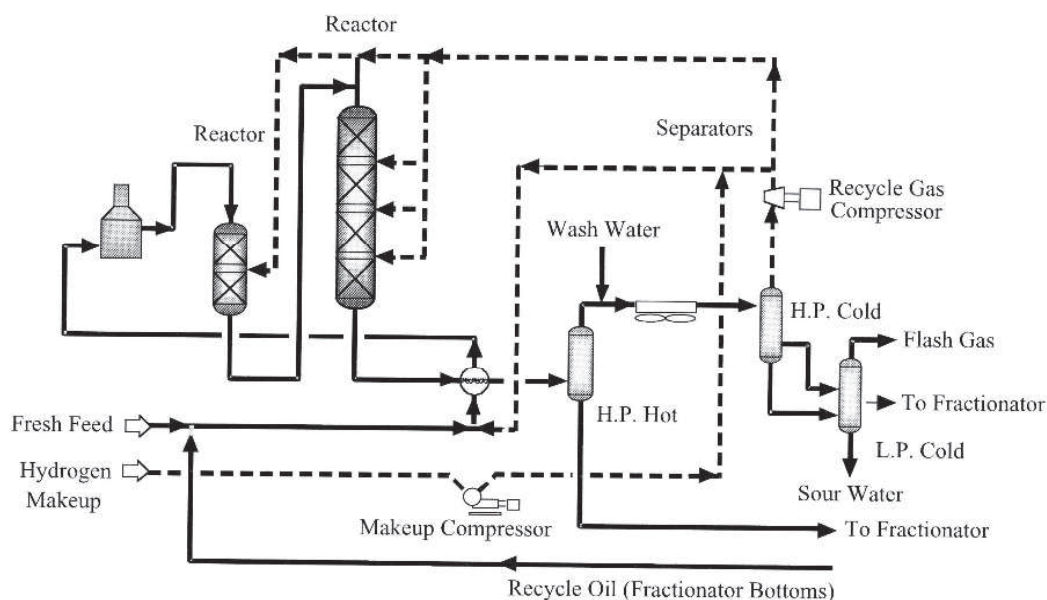
The products from hydrocracking units are composed of either saturated or aromatic compounds; no olefins are found. In making gasoline, the lower paraffins formed in the reaction have high octane numbers. The remaining gasoline has excellent properties as a feed to catalytic reforming, producing a highly aromatic gasoline, which easily attains 100 octane number. Another attractive feature of hydrocracking is the low yield of gaseous components, such as methane, ethane, and propane, which are less desirable than gasoline.

A hydrocracking unit may have either a single stage once-through, single stage with recycle, or a two-stage flow scheme. Among these flow schemes both single stage with recycle and two-stage recycle are widely used in the industry.

### 8.10.1 Single Stage with Recycle

The flow diagram of a single stage with recycle unit is shown in Fig. 8.24. The fresh feed is mixed with the recycled oil, preheated and passed downward through the reactor over the catalyst bed along with hydrogen. The effluent from the reactor goes through a series of separator to recover various product fractions and

hydrogen. The recovered hydrogen together with the make up hydrogen is recycled back to the reactor. Both the pre-treatment and cracking are achieved in the same reactor using amorphous catalyst. However most of the units use a pretreatment and a cracking catalyst configuration. The stream first passes through the pre-treatment catalyst where organic sulfur and nitrogen are converted to hydrogen sulfide and ammonia, respectively. No attempt is made to remove hydrogen sulfide and ammonia from the feed stream at this point. The product from the first catalyst bed is passed over the hydrocracking catalyst in the second stage of the reactor where most of the hydrocracking takes place. Hydrogen sulfide and ammonia have little effect on the conversion or yield of the final product. The catalyst for hydrocracking consists of sulfided molybdenum and nickel on alumina support. The reactor operates in the temperature range of 570–800°F (300–425°C) and hydrogen pressures between 1,250 and 2,500 psig (85–170 bar).

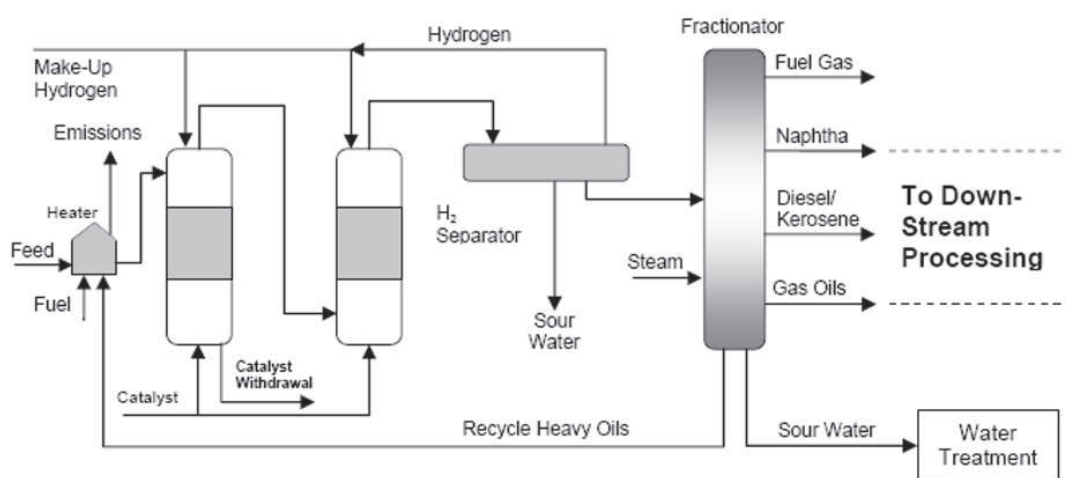


**Fig. 8.24.** Single stage hydrocracking unit. (From W. Letzsch, Fluid catalytic cracking, Chapter 6, Handbook of Petroleum Processing, Eds. DSJ Jones and PR Pujado, Springer, 2006 [132]).

### 8.10.2 Two-Stage Process

In the two stage process, the hydrotreatment is carried out in the first stage. Pre-heated feedstock, along with recycled hydrogen is sent to the first-stage reactor, where sulfur and nitrogen compounds are converted to hydrogen sulfide and ammonia over a catalyst. Limited hydrocracking also occurs. A schematic diagram of the two-stage process is shown in Fig. 8.25.

The product stream from the first stage is cooled and liquefied, and thus separates hydrogen sulfide and ammonia. The liquid stream is run through a hydrocarbon separator where it is fractionated with the unconverted oil and is recycled to the second stage. The hydrogen is recycled to the feedstock. Depending on the products desired, the stream is separated into gasoline components, jet fuel, and gas oil fractions. The bottom products are again mixed with a hydrogen stream and charged to the second stage. A higher temperature and pressure is used in the second reactor. The product from the second stage is separated from the hydrogen and charged to the fractionator. Since hydrogen sulfide and ammonia are not present in the feed stream to the second stage reactor, various noble metal or base metal sulfide can be used for hydrocracking. Typical reactions that take place during hydrocracking are given in the handbook [173].



**Fig. 8.25.** Two stage hydrocracking unit. (Adapted from 2006 Refining Processes Handbook, Hydrocarbon Processing, Gulf Publishing Co. Houston, USA [173]).

## 8.11 Hydrotreatment

The main objective of hydrotreatment is to remove various undesired compounds such as sulfur, nitrogen, olefins, and aromatics from the petroleum fractions [174–184]. Hydrotreatment is also used to upgrade and to meet the strict product specifications or for use as feedstocks elsewhere in the refinery. The product quality specifications are driven by environmental regulations. A hydrotreatment facility is designed to employ a wide range of operating conditions due to the variation of the type of feed, desired cycle length, and expected quality of the finished product. The following fractions are generally hydrotreated:

- **Naptha:** Pretreatment of the feed prior to catalytic reforming to remove sulfur, nitrogen and metals. The trace metals present in the stream would poison (deactivate) the noble metal catalysts used in the reforming units.
- **Kerosene and Diesel:** Hydrotreatment of this fraction removes sulfur, saturates olefins and some aromatics in the fraction. This upgrades kerosene and diesel in terms of its product quality and stability.
- **Lube oil:** Hydrotreatment improves its viscosity index, color and stability.
- **FCC Feed:** Removal of sulfur and nitrogen compounds through hydrotreatment improves yield, reduces emissions, and extends catalyst life.
- **Resids:** Hydrotreatment removes sulfur compounds and improves its quality as feedstocks.

Although hydrotreatment is used for a variety of applications as described above, the basic flow diagram of the hydrotreatment plant is common. The two major sections of the plant are a high-pressure reactor system (Fig. 8.26) and a low-pressure fractionation system (Fig. 8.27).

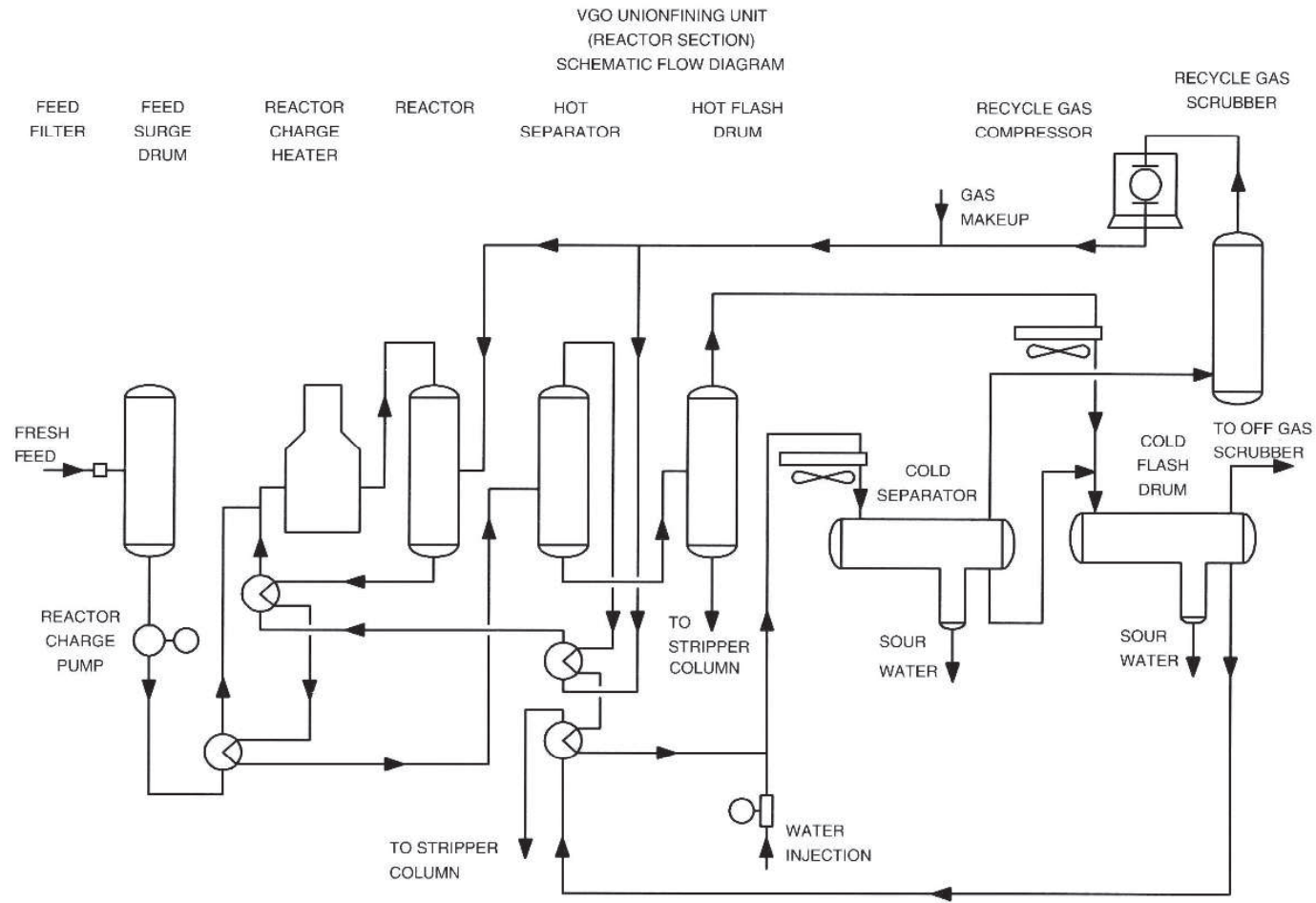
The typical operating conditions of a hydrotreatment plant are as follows:

LHSV:	0.2–8.0
H <sub>2</sub> circulation rate:	300–4,000 SCFB (50–675 Nm <sup>3</sup> /m <sup>3</sup> )
H <sub>2</sub> partial pressure:	200–2,000 psia (14–138 bar)
SOR temperature:	550–700°F (290–370°C)

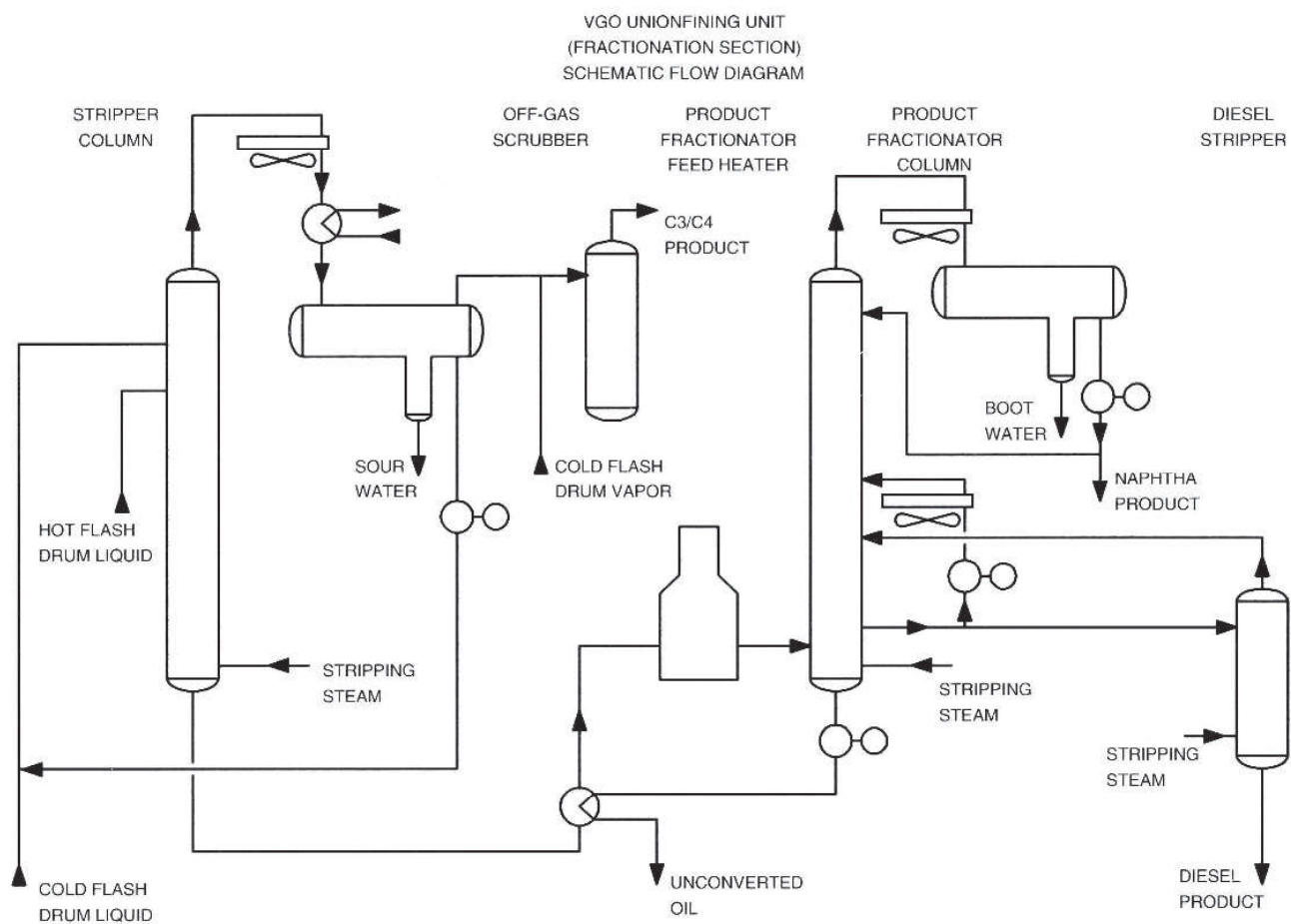
(LHSV: Liquid Hourly Space Velocity)

The feed and recycled gas (reactants) streams are heated to the desired temperature before introducing them to the top of the reactor. As the reactants flow downward through the catalyst bed, the hydrogenation reactions take place. The effluents from the reactor are forwarded to the fractionation sections where the stream is separated to desired products. The gaseous effluent from the reactor contains H<sub>2</sub> and H<sub>2</sub>S. The H<sub>2</sub>S is removed from the stream before recycling back to the feed stream. Typical chemical reactions that take place in the reactor are given in [173].

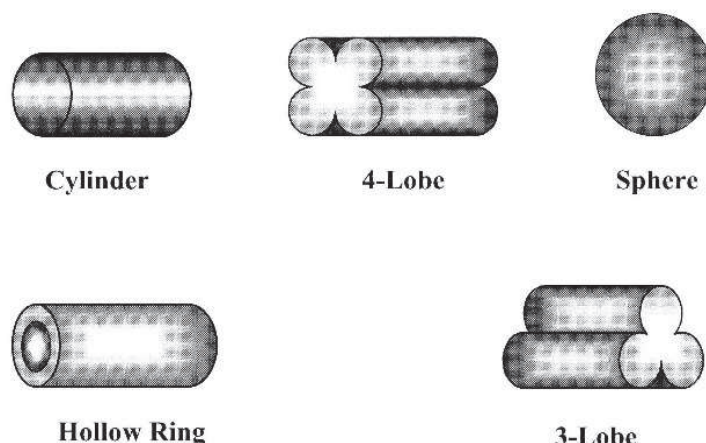
Hydrotreatment catalysts come in different shapes and sizes as shown in Fig. 8.28, however, their basic characteristics are similar. The active component of the catalyst is generally molybdenum sulfide, which is about 25 wt%, of the total mass. The active component is dispersed on an inert support such as  $\gamma$ -alumina. A promoter, which may be up to 25 wt%, is added to the catalyst to enhance the activity of molybdenum sulfide. Both cobalt–molybdenum (Co–Mo) and nickel–molybdenum (Ni–Mo) have been used as a promoter.



**Fig. 8.26.** The high pressure reactor system for hydrotreatment (W. Letzsch, Fluid catalytic cracking, Chapter 6, Handbook of Petroleum Processing, Eds. DSJ Jones and PR Pujado, Springer, 2006).



**Fig. 8.27.** The low pressure fractionation system of the hydrotreatment unit (W. Letzsch, Fluid catalytic cracking, Chapter 6, Handbook of Petroleum Processing, Eds. DSJ Jones and PR Pujado, Springer, 2006).



**Fig. 8.28.** Various shapes of hydrotreatment catalysts. (From W. Letzsch, Fluid catalytic cracking, Chapter 6, Handbook of Petroleum Processing, Eds. DSJ Jones and PR Pujado, Springer, 2006).

## 8.12 Gasoline Reforming

Gasoline reforming is referred to altering the composition of gasoline to achieve a higher octane rating [185–201]. Various gasoline or motor fuel fractions from different parts of the refinery are further processed to ensure the product quality specifications. Three major processes are used for gasoline reforming:

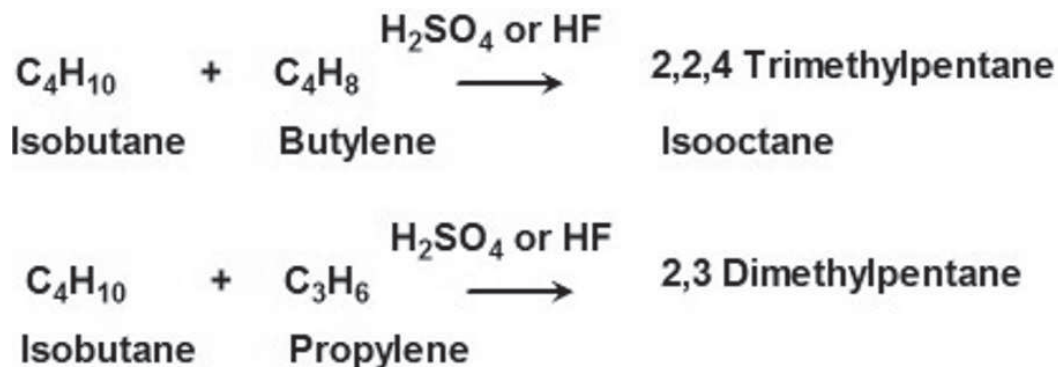
- Alkylation
- Catalytic olefin condensation
- Isomerization

### 8.12.1 Alkylation

Alkylation of motor fuel is carried out to produce highly branched C5–C12 isoparaffins (also called alkylate) which are valuable gasoline blending component. Alkylate is an ideal blendstock for making high octane fuel, especially as the alternatives, such as lead additives, are banned and other additives such as MTBE and aromatics are under scrutiny in many countries due to various environmental and health concerns. In this process, C3–C5 olefins along with isobutane are converted to C5–C12 isoparaffins using an acid catalyst. Either a liquid or a solid acid may be used as a catalyst. A number of catalysts including  $\text{H}_2\text{SO}_4$ , HF,  $\text{H}_2\text{SO}_4\text{-HSO}_3\text{F}$ ,  $\text{HF-BF}_3$ ,  $\text{AlCl}_3\text{-HCl}$ , trifluoromethane sulfonic acid chloride, Pt-alumina,  $\text{BF}_3$  on alumina, zeolites, and ion exchanged resins have been proposed for the



alkylation reactions. Among these catalysts, HF [202–206] and H<sub>2</sub>SO<sub>4</sub> [207–219] alkylation are most common in the refineries. Recently, UOP has developed a solid catalyst alkylation process (Alkylene<sup>TM</sup>) that is available for commercial applications. Typical reactions are shown below. The majority of alkylate produced today comes from two routes: sulfuric and hydrofluoric acid catalyzed alkylation. The typical alkylation reactions are shown below.



### 8.12.1.1 Hydrofluoric Acid Alkylation Process

The basic operating principle of sulfuric and hydrofluoric alkylation processes is rather similar. However, sulfuric acid is not as active as hydrofluoric acid as catalyst for the alkylation reaction.

Sulfuric acid alkylation reaction should be carried out at a very low temperature to maintain a low reactor temperature. The sulfuric acid consumption rate during alkylation reaction is over hundred times that of HF.

A schematic flow diagram of the UOP HF Alkylation process is shown in Fig. 8.29. The UOP design is a forced acid and water cooled system. In this process, water is used to remove the heat of reaction. Therefore, the acid requirement is not dependent on the heat removal and the acid use could be reduced significantly. The mixing between the hydrocarbon and the acid is accomplished using a pump, which at the same time can provide necessary inlet pressure for feed nozzles. The feed is introduced in the alkylation reactor as fine droplets. The enhanced dispersion and contact of hydrocarbon and acid contribute an additional 0.2–0.7 octane to the alkylate product. In the last 6 years UOP has licensed 6 new HF units.

### 8.12.1.2 Sulfuric Acid Alkylation Process

ExxonMobil introduced the stirred auto-refrigerated sulfuric acid alkylation process to maximize the yield. A simplified flow diagram of the process is shown in Fig. 8.30.

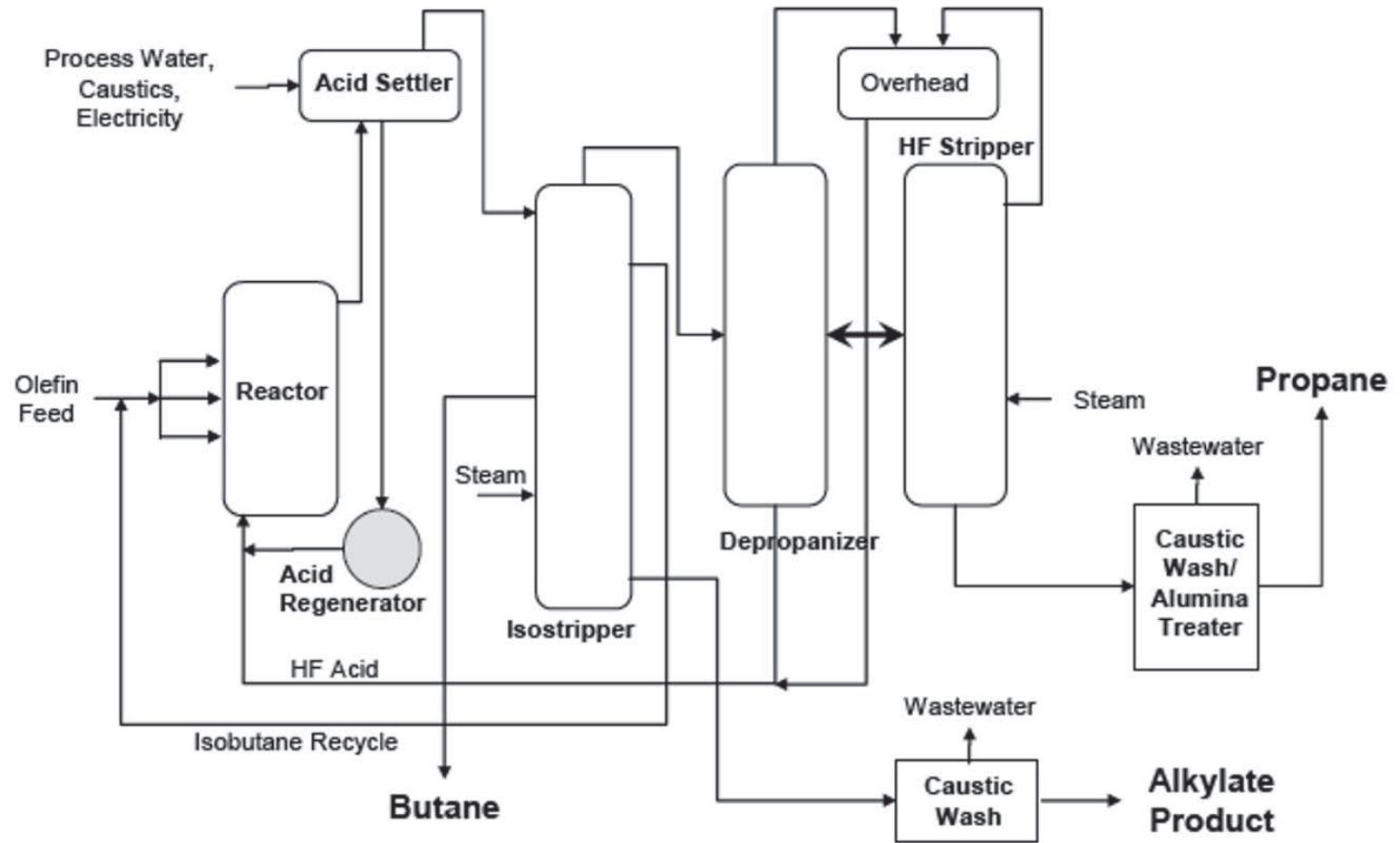


Fig. 8.29. The UOP hydrofluoric acid catalyzed alkylation process (2006 Refining Processes Handbook, Hydrocarbon Processing, 2006 [173]).

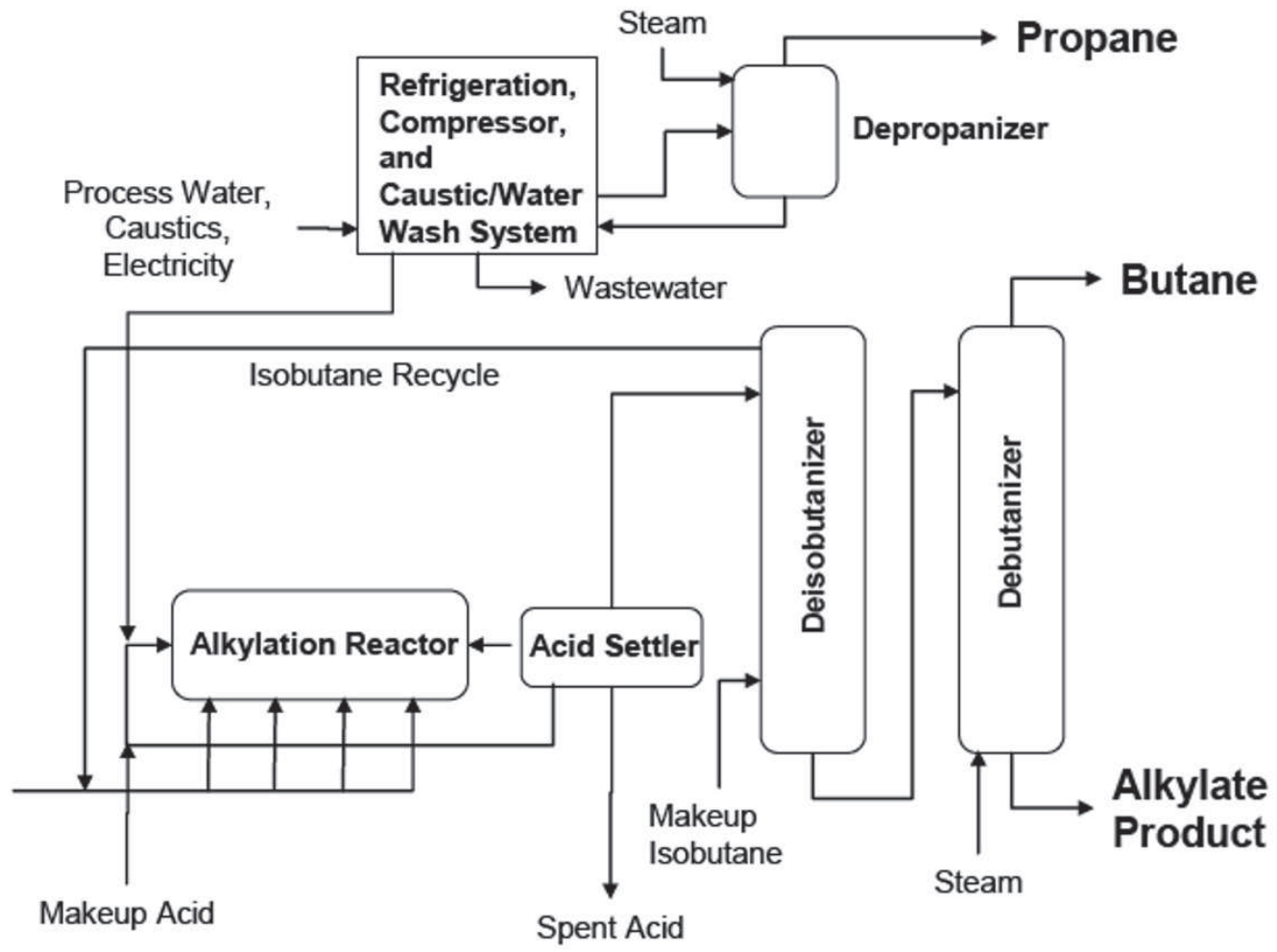


Fig. 8.30. Sulfuric acid catalyzed alkylation process flow diagram (2006 Refining Processes Handbook, Hydrocarbon Processing, 2006 [173]).

In this process, the olefin-recycle isobutane mixture, along with recycle acid and recycle refrigerant, are introduced to the reactor system. An emulsion is created through thorough mixing of reactants and the acid catalyst. The olefins and isobutane react very quickly to form alkylate and release reaction heat. The reaction heat is removed by the auto-refrigeration system by vaporizing some isobutane from the reaction mixture. Just like any other refrigeration system, the iso-butane vapor is compressed, condensed, and returned to the reactor as recycle refrigerant. From the reactor, the emulsion is routed to the settler, where the acid is separated from the hydrocarbon phase, then recycled back to the reactor. The hydrocarbon stream is washed with water to remove acidic components and is fed to the deisobutanizer. The deisobutanizer bottom stream is split further into normal butane and alkylates products.

A comparison of the two alkylation processes is given in Table 8.13. The HF catalyzed process is cheaper to sulfuric acid process.

**Table 8.13.** A comparison of alkylation processes.

<b>Process Parameters</b>	<b>Alkylene + Butamer*</b>	<b>HF+ Butamer*</b>	<b>Onsite Regeneration H<sub>2</sub>SO<sub>4</sub> +Butamer*</b>
Total feed from FCC, BPSD	7, 064	7, 064	7, 064
C5+ Alkylate	8, 000	7, 990	7, 619
C5+ Alkylate RON	95.0	95.2	95.0
MON	92.9	93.3	92.2
(R+M)/2	94.0	84.3	93.6
C5+ Alkylate D-86, °F			
50%	213	225	216
90%	270	290	296
Economics			
Variable cost of Production, \$/bbl**	2.57	0.82	1.37
Fixed cost of production	1.88	2.43	3.53
Total cost of production	4.45	3.25	4.90
EEC, SMM	46.5	40.5	63.3

All cases include a butamer to maximize feed utilization

Raw materials are not included

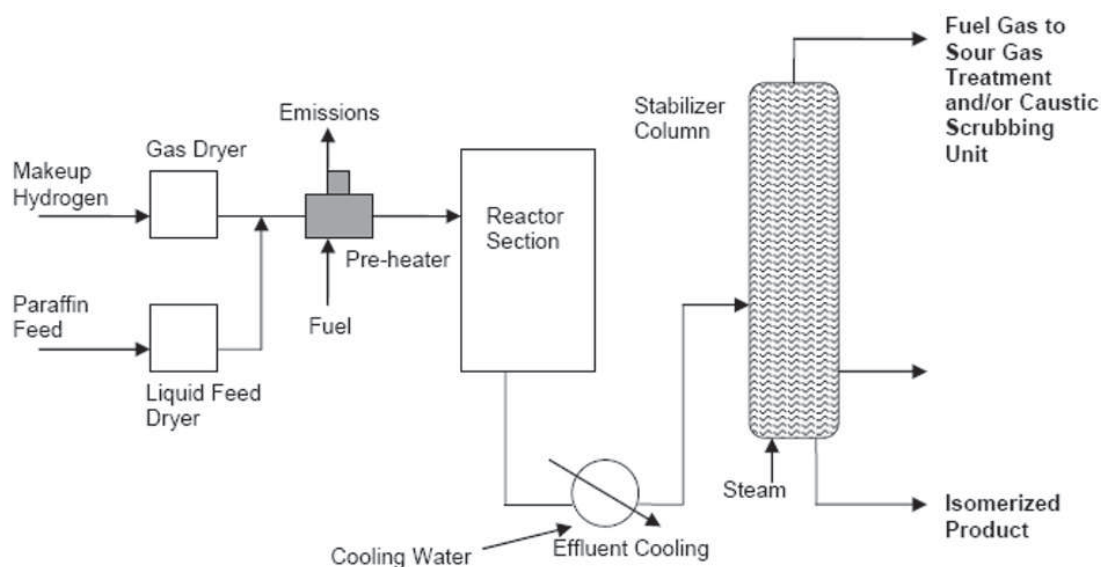
### **8.12.2 Isomerization Process**

Isomerization of n-butane, n-pentane and n-hexane is carried out into their respective isoparaffins so that substantially higher octane number products are produced.

Isomerization process can also provide additional feedstock for alkylation unit since it converts n-butane into isobutene.

There are two distinct isomerization processes; butane (C4) and pentane/hexane (C5/C6). Butane isomerization produces feedstock for alkylation. Aluminum chloride catalyst and hydrogen chloride are universally used for the low-temperature processes. Platinum or another metal catalyst is used for the higher-temperature processes. In a low-temperature process, the reactor operates at 230–340°F and 200–300 psi. Hydrogen is removed in a high-pressure separator and hydrogen chloride is recovered in a stripper column. The resultant butane mixture is sent to a fractionator (deisobutanizer) to separate n-butane from the isobutane product.

In Pentane/hexane isomerization process, dried and desulfurized feedstock is mixed with a small amount of organic chloride and recycled hydrogen, and then heated in a reactor. The feed next goes to the isomerization reactor where the paraffins are isomerized to isoparaffins in the presence of another catalyst. The reactor effluent is then cooled and separated into a liquid product (isomerate) and a recycle hydrogen-gas stream. The flow diagram of an isomerization unit is shown in Fig. 8.31.



**Fig. 8.31.** A schematic process flow diagram of the isomerization process (From 2006 Refining Processes Handbook, Hydrocarbon Processing, 2006 [173]).

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## Listing of Standards

### European Standard

- EN 116: Diesel and domestic heating fuels – Determination of cold filter plugging point
- EN 237: Liquid petroleum products – Petrol – Determination of low lead concentrations by atomic absorption spectrometry
- EN 1601: Liquid petroleum products – Unleaded petrol – Determination of organic oxygenate compounds and total organically bound oxygen content by gas chromatography (O-FID)
- EN 2160: Petroleum products – Corrosiveness to copper – Copper strip test (ISO 2160:1998)
- EN 3104: Petroleum products – Transparent and opaque liquids – Determination of kinematic viscosity and calculation of dynamic viscosity (ISO 3104:1994)
- EN 3405: Petroleum products - Determination of distillation characteristics at atmospheric pressure (ISO 3405:2000)
- EN 3675: Crude petroleum and liquid petroleum products – Laboratory determination of density – Hydrometer method (ISO 3675:1998)
- EN 4264: Petroleum products - Calculation of cetane index of middle-distillate fuels by the four-variable equation (ISO 4264:2007)
- EN 5165: Petroleum products – Determination of the ignition quality of diesel fuels – Cetane engine method (ISO 5165:1998). EN ISO 5165:1998
- EN 6245: Petroleum products – Determination of ash (ISO 6245:2001) EN ISO 6245:2002
- EN 6246: Petroleum products – Gum content of light and middle distillate fuels – Jet evaporation method (ISO 6246:1995)
- EN 7536: Petroleum products – Determination of oxidation stability of gasoline – Induction period method (ISO 7536:1994)
- EN 8754: Petroleum products – Determination of sulfur content – Energy-dispersive X-ray fluorescence spectrometry (ISO 8754:2003)
- EN 10370: Petroleum products – Determination of carbon residue – Micro method (ISO 10370:1993). EN ISO 10370:1995
- EN 12177: Liquid petroleum products – Unleaded petrol – Determination of benzene content by gas chromatography. EN 12177:1998/AC:2000
- EN 12185: Crude petroleum and petroleum products – Determination of density – Oscillating U-tube method (ISO 12185:1996)
- EN 12205: Petroleum products – Determination of the oxidation stability of middle-distillate fuels (ISO 12205:1995)
- EN 12662: Liquid petroleum products – Determination of contamination in middle distillates



- EN 12916: Petroleum products – Determination of aromatic hydrocarbon types in middle distillates – High performance liquid chromatography method with refractive index detection
- EN 12937: Petroleum products – Determination of water – Coulometric Karl Fischer titration method (ISO 12937:2000)
- EN 13016-1: Liquid petroleum products – Vapour pressure – Part 1: Determination of air saturated vapour pressure (ASVP) and calculated dry vapour pressure equivalent (DVPE)
- EN 13016-2: Liquid petroleum products – Vapour pressure – Part 2: Determination of absolute pressure (AVP) between 40°C and 100°C
- EN 14596: Petroleum products – Determination of sulfur content – Wavelength-dispersive X-ray fluorescence spectrometry (ISO 14596:2007)
- EN 22719: Petroleum products and lubricants; determination of flash point; Pensky-Martens closed cup method (ISO 2719:1988)
- EN 23015: Petroleum products – Determination of cloud point (ISO 3015:1992)
- EN 24260: Petroleum products and hydrocarbons – Determination of sulfur content – Wickbold combustion method (ISO 4260:1987)
- EN 25163: Motor and aviation-type fuels – Determination of knock characteristics – Motor method
- EN 25164: Methods of test for petroleum and its products. Motor fuels. Determination of knock characteristics. Research method (1994)

### **Institute of Petroleum Standards**

- IP 4: Petroleum products – Determination of Ash IP 30 (2005)
- IP 40: Petroleum products – Determination of oxidation stability of gasoline – Induction period method (1997)
- IP 41: Petroleum products – Determination of the ignition quality of diesel fuels – Cetane engine method (1999)
- IP 69: Petroleum products – Determination of vapour pressure – Reid method (2001)
- IP 71: Section 1: Petroleum products – Transparent and opaque liquids – Determination of kinematic viscosity and calculation of dynamic viscosity. (1995) Section 2: Glass capillary kinematic viscometers – Specifications and operating instructions (1997)
- IP 123: Petroleum products – Determination of distillation characteristics at atmospheric pressure (2001)
- IP 131: Petroleum products – Gum content of light and middle distillate fuels – Jet evaporation method (1999)
- IP 154: Petroleum products – Corrosiveness to copper – Copper strip test (2000)
- IP 156: Determination of hydrocarbon types in petroleum products – Fluorescent indicator adsorption method (2008)
- IP 160: Crude petroleum and liquid petroleum products – Laboratory determination of density – Hydrometer method IP 219 Cloud Point of Petroleum Products (1999)
- IP 236: Petroleum products – Determination of knock characteristics of motor and aviation fuels – Motor method (2006)
- IP 237: Petroleum products – Determination of knock characteristics of motor fuels – Research method (2006)
- IP 243: Petroleum products and hydrocarbons – Determination of sulfur content – Wickbold combustion method (1994)
- IP 309: Diesel and domestic heating fuels – Determination of cold filter plugging point (1999)

- IP 336: Petroleum products – Determination of sulfur content – Energy-dispersive-X-ray fluorescence method (2004)
- IP 342: Petroleum products – Determination of thiol (mercaptan) sulfur in light and middle distillate fuels – Potentiometric method (2000)
- IP 365: Crude petroleum and petroleum products – Determination of density – Oscillating U-tube method (1997)
- IP 380: Petroleum products – Calculation of cetane index of middle distillate fuels by the four-variable equation (2008)
- IP 388: Petroleum products – Determination of the oxidation stability of middle-distillate fuels (1997)
- IP 391: Petroleum products – Determination of aromatic hydrocarbon types in middle distillates – High performance liquid chromatography method with refractive index detection (2007)
- IP 394: Liquid petroleum products – Vapour pressure – Part 1: Determination of air saturated vapour pressure (ASVP) (2008)
- IP 398: Petroleum products – Determination of carbon residue – Micro method (1996)
- IP 408: Liquid petroleum products – Unleaded petrol – Determination of organic oxygenate compounds and total organically bound oxygen content by gas chromatography (O-FID) (1998)
- IP 425: Liquid petroleum products – Unleaded petrol – Determination of benzene content by gas chromatography (2001)
- IP 428: Liquid petroleum products – Petrol – Determination of low lead concentrations by atomic absorption spectrometry (2006)
- IP 440: Liquid petroleum products – Determination of contamination in middle distillates (1999)
- IP 447: Petroleum products – Determination of sulfur content – Wavelength-dispersive X-ray fluorescence spectrometry (2008)
- IP 450: Diesel fuel – Assessment of lubricity using the high-frequency reciprocating rig (HFRR) – Part I: Test Method (2000)
- IP 490: Petroleum products – Determination of sulfur content of automotive fuels – Ultra-violet fluorescence method (ISO 20846:2004) (2005)

### **International Organization for Standards (ISO)**

- ISO 2160: Petroleum products – Corrosiveness to copper – Copper strip test Edition: 3 (1998)
- ISO 2719: Determination of flash point – Pensky-Martens closed cup method Edition: 3 (2002)
- ISO 3007: Petroleum products and crude petroleum – Determination of vapour pressure – Reid method (1999)
- ISO 3012: Petroleum products – Determination of thiol (mercaptan) sulfur in light and middle distillate fuels – Potentiometric method (1999)
- ISO 3015: Petroleum products – Determination of cloud point (1992)
- ISO 3104: Petroleum products – Transparent and opaque liquids – Determination of kinematic viscosity and calculation of dynamic viscosity (1994)
- ISO 3405: Petroleum products – Determination of distillation characteristics at atmospheric pressure (2000)
- ISO 3675: Crude petroleum and liquid petroleum products – Laboratory determination of density – Hydrometer method (1998)

- ISO 3837: Liquid petroleum products – Determination of hydrocarbon types – Fluorescent indicator adsorption method (1993)
- ISO 4260: Petroleum products and hydrocarbons – Determination of sulfur content – Wickbold combustion method (1987)
- ISO 4264: Petroleum products and hydrocarbons – Determination of sulfur content Wickbold combustion method (2007)
- ISO 5163: Petroleum products – Determination of knock characteristics of motor and aviation fuels – Motor method (2005)
- ISO 5164: Petroleum products – Determination of knock characteristics of motor fuels – Research method (2005)
- ISO 5165: Petroleum products – Determination of the ignition quality of diesel fuels – Cetane engine method (1998)
- ISO 6245: Petroleum products – Determination of ash (2001)
- ISO 6246: Petroleum products – Gum content of light and middle distillate fuels – Jet evaporation method (1995)
- ISO 7536: Petroleum products – Determination of oxidation stability of gasoline – Induction period method (1994)
- ISO 8754: Petroleum products – Determination of sulfur content – Energy-dispersive X-ray fluorescence spectrometry (2003)
- ISO 10370: Petroleum products – Determination of carbon residue – Micro method (1993)
- ISO 12156: Diesel fuel – Assessment of lubricity using the high-frequency reciprocating rig (HFRR) – Part 1: Test method. (2007) Diesel fuel – Assessment of lubricity using the high-frequency reciprocating rig (HFRR) – Part 2: Limit (2006)
- ISO 12185: Crude petroleum and petroleum products – Determination of density – Oscillating U-tube method (1996)
- ISO 12205: Petroleum products – Determination of the oxidation stability of middle-distillate fuels (1995)
- ISO 12937: Petroleum products – Determination of water – Coulometric Karl Fischer titration method (2000)
- ISO 14596: Petroleum products – Determination of sulfur content – Wavelength-dispersive X-ray fluorescence spectrometry (2007)

### **American Society for Testing and Materials (ASTM)**

- ASTM D86 07 Standard Test Method for Distillation of Petroleum Products at Atmospheric Pressure
- ASTM D93 06 Standard Test Methods for Flash Point by Pensky-Martens Closed Cup Tester
- ASTM D130 -04 Standard Test Method for Corrosiveness to Copper from Petroleum Products by Copper Strip Test
- ASTM D323 06 Standard Test Method for Vapor Pressure of Petroleum Products (Reid Method)
- ASTM D381 04 Standard Test Method for Gum Content in Fuels by Jet Evaporation
- ASTM D445 04 Standard Test Method for Kinematic Viscosity of Transparent and Opaque Liquids (and the Calculation of Dynamic Viscosity)
- ASTM D482 07 Standard Test Method for Ash from Petroleum Products
- ASTM D525 01 Standard Test Method for Oxidation Stability of Gasoline (Induction Period Method)

- ASTM D613 05 Standard Test Method for Cetane Number of Diesel Fuel Oil
- ASTM D1298 99 Standard Test Method for Density, Relative Density (Specific Gravity), or API Gravity of Crude Petroleum and Liquid Petroleum Products by Hydrometer Method
- ASTM D1319 03 Standard Test Method for Hydrocarbon Types in Liquid Petroleum Products by Fluorescent Indicator Adsorption
- ASTM D1319 03e1 Standard Test Method for Hydrocarbon Types in Liquid Petroleum Products by Fluorescent Indicator Adsorption
- ASTM D2274 03 Standard Test Method for Oxidation Stability of Distillate Fuel Oil (Accelerated Method)
- ASTM D2500 05 Standard Test Method for Cloud Point of Petroleum Products
- ASTM D2622 08 Standard Test Method for Sulfur in Petroleum Products by Wavelength Dispersive X-ray Fluorescence Spectrometry
- ASTM D2699 07 Standard Test Method for Research Octane Number of Spark-Ignition Engine Fuel
- ASTM D2700 07 Standard Test Method for Motor Octane Number of Spark-Ignition Engine Fuel
- ASTM D3227 04 Standard Test Method for (Thiol Mercaptan) Sulfur in Gasoline, Kerosine, Aviation Turbine, and Distillate Fuels (Potentiometric Method)
- ASTM D3237 -06 Standard Test Method for Lead in Gasoline by Atomic Absorption Spectroscopy
- ASTM D3606 07 Standard Test Method for Determination of Benzene and Toluene in Finished Motor and Aviation Gasoline by Gas Chromatography
- ASTM D4052 96(2002)e1 Standard Test Method for Density and Relative Density of Liquids by Digital Density Meter
- ASTM D4530 07 Standard Test Method for Determination of Carbon Residue (Micro Method)
- ASTM D4294 08 Standard Test Method for Sulfur in Petroleum and Petroleum Products by Energy Dispersive X-ray Fluorescence Spectrometry
- ASTM D4737 04 Standard Test Method for Calculated Cetane Index by Four Variable Equation
- ASTM D4952 02(2007) Standard Test Method for Qualitative Analysis for Active Sulfur Species in Fuels and Solvents (Doctor Test)
- ASTM D5191 07 Standard Test Method for Vapor Pressure of Petroleum Products (Mini Method)
- ASTM D5453 08 Standard Test Method for Determination of Total Sulfur in Light Hydrocarbons, Spark Ignition Engine Fuel, Diesel Engine Fuel, and Engine Oil by Ultraviolet Fluorescence
- ASTM D5769 04 Standard Test Method for Determination of Benzene, Toluene, and Total Aromatics in Finished Gasolines by Gas Chromatography/Mass Spectrometry
- ASTM D6079 04 Standard Test Method for Evaluating Lubricity of Diesel Fuels by the High-Frequency Reciprocating Rig (HFRR)
- ASTM D6371 05 Standard Test Method for Cold Filter Plugging Point of Diesel and Heating Fuels

ASTM D5599 00 Standard Test Method for Determination of Oxygenates in Gasoline by Gas Chromatography and Oxygen Selective Flame Ionization Detection

ASTM D6217 98(2003)e1 Standard Test Method for Particulate Contamination in Middle Distillate Fuels by Laboratory Filtration

ASTM D6304 04 Standard Test Method for Determination of Water in Petroleum Products, Lubricating Oils, and Additives by Coulometric Karl Fisher Titration

## Problems

1. In Table 8.1 is given a list of products which are manufactured from petroleum based products. Is there any alternative route for their manufacturing? Do you think the prices and quality of these products will be the same? What impact will this have on our society.
2. What is crude oil benchmarking? Why it is necessary?
3. Why is it important to characterize crude oil?
4. Is crude oil essential for all types of transportation? Which sector of the transportation system could be run without petroleum and how?
5. What are various processes involved in the processing of crude oil and what are their objectives?
6. Why is crude petroleum separated into various fractions?
7. How dependent is the United States on foreign oil?
8. How many barrels of oil does the United States consume per year?
9. How much oil is produced in Alaska and where does it go?
10. How much petroleum does the United States import?
11. Why don't fuel prices change as quickly as crude oil prices?
12. Do we have enough oil worldwide to meet our future needs?
13. How many gallons of gasoline does one barrel of oil make?
14. What are the differences between various types of crude oil prices?
15. What are the differences among "crude oil", "petroleum products", and "petroleum"?
16. What are the products and uses of petroleum?
17. When was the last refinery built in the United States?
18. Define the octane number? Why is it important?
19. Write a report on the energy requirements for operating a refinery.
20. Write a report on the wastes generated from processing of crude oil.
21. What is the difference between gasoline and diesel fuel?