History of Modern Chemical Industries

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In an earlier edition, a history of chemical technology was presented from ancient times till about 1900. Much of this history is inseparable from history of alchemy, of chemical magic, and traditional practices. Ancient witch doctors, shamans, could treat sick people and cure some of them through their knowledge of special chemicals obtained from botanical and other sources. What we usually refer to as modern science originated in Europe during the 17th century, and continued with the Age of Reason (18th Century) till the birth of the New Sciences (Quantum Mechanics, Relativity, New Biology etc.). Many of the stalwarts during this period, esp. Davy, Lavoisier, Faraday, Priestley, Scheele, Berzelius, Ostwald were motivated by the need to produce materials which may provide food, clothing, shelter and better health to mankind. Removed as we are by at least one century from these persons (in some cases, by more than a century), we cannot even imagine the hardships they had to overcome, to meet the challenges they set before themselves—usually always with the idea that their work will benefit humanity. I say 'usually' because there were, again, always a few individuals who were driven more by the prospect of personal (monetary or otherwise) gain.

Let us recall very briefly the situation from early days of the industry till about 1900. Most of the changes that are really important happened during the 18th Century, in the latter half of it to be precise. The first chemical industry happened with the Leblanc process for making caustic soda (NaOH). Nicholas Leblanc (1742-1806) was the physician of Duke of Orleans. He devised this method in 1787 and obtained a patent for it four years later. In 1874, the world production of caustic soda was 0.525 Mtonnes, more than 94% of it made by the Leblanc process. However, in 1902, the world production was 1.8 Mtonnes, but only about 8.3% of it was made by this process. By then other processes e.g. electrolytic process were invented (1875-1900). An important point is that the Leblanc process was never important in the New World, as it was cheaper to import European NaOH in North America, and by the time chemical industry developed there, the electrolytic process was already invented.

Ironmaking was in existence since prehistory. Even now, there are tribes making iron tools using ground iron ore, coal etc. in bamboo and other containers. By 16-17th Century, people in Europe were using batch process, with small blast furnaces in outhouses, with charcoal as the burner and reducing agent. Around 1773, Abraham Darby in West England developed a process for making coke from coal, and used this instead of charcoal in his blast furnace in Shropshire. Charcoal making was time consuming. The new method revolutionised ironmaking, and in succeeding decades iron from this area was used

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in making steam engines, rails, boats and ships, building structures etc. for the first time. The method was still primitive. Traditionally, the output or pig iron from these foundries was made into wrought iron by manually mixing with iron ore and charcoal. Steel making was essentially small scale and expensive, using either the cementation or crucible processes, where the iron was mixed with charcoal and impurities burnt out. These were batch processes. Only from mid 19th Century, steel-making became a major industry because of the Bessemer and Open Hearth processes. In both, air and silica or other lining in the furnace was used to lower the carbon content, and remove impurities as acidic or basic slag. The slag was used to make cement, among other items. These processes have been superseded by Electric Arc (1878, Siemens) and Basic Oxygen (1952) processes. Major producers of iron ore are China, Brazil, former USSR, Australia, India and USA, roughly in that order, whereas major steel producers are Western Europe, North America, Japan, China, former USSR and South America, again in that order. These change somewhat due to mergers and acquisitions of multinational corporations.

No discussion on chemical industries is complete without mentioning two (or three) chemicals, which together constitute 90% of the industry. These are (1) sulphuric acid, (2) ammonia, and (3) superphosphate or phosphatic fertilisers. Sulfuric acid is the world's most important industrial chemical, i.e., the largest chemical produced by weight per year. Concentrated sulphuric acid, called "oil of vitriol" earlier, was made by distillation of green vitriol, hydrated ferrous sulphate. This was replaced by a process patented by Joshua Ward in England in 1749, where sulphur and Chile saltpetre (sodium nitrate) was burnt together in vessels with water. Although the method was used in Europe much earlier, the new method became popular and the price came down from 2/lb to 2 shillings/lb. John Roebuck replaced glass jars by lead chambers in 1755. This brought price down further. Clement and a co-worker discovered in 1793 in France that if air is admitted, less nitrate is needed in the process. This reduced the cost even further. However, the modern method uses contact process, patented by Philips in 1831, where SO_2 is converted to SO_3 by platinum catalyst, and purity can be improved beyond the 78% limit earlier. Today, K_2SO_4 promoted vanadium oxide catalyst is used.

Industrial ammonia was produced from 1913 in Germany, using the then new Haber-Bosch process of high pressure catalytic conversion of N_2 and H_2. Hydrogen was then obtained by electrolysis of water, but is now made by coke and water vapour, or from natural gas, or from naphtha. Most of the ammonia produced is used in fertilisers, either directly (28.7%), or as urea (22.4%), ammonium nitrate (15.8%), ammonium phosphates (14.6%) and ammonium sulphate (3.4%) Rest of it is used to make explosives and polymers, in refrigeration and wood pulping, as rubber stabiliser, to control pH, in food and beverages and in pharmaceuticals. Although by weight, ammonia produced per year is less than sulphuric acid (by a factor of nearly half), the amount produced in moles is about 4 times, as the molecular weight of ammonia is much less vis-a-vis H_2SO_4.

Phosphates are ubiquitous as industrial and domestic chemicals, but are often overlooked. Only a few of their applications are listed here. For example, sodium phosphate is used as a strong cleaning agent; in combination with NaOCl, it is used as a bleach, antibacterial and dishwashing chemical. Sodium hydrogen phosphate is used as a buffer, as a cheese emulsifier, for picking of meat, in instant pudding and gels, and in breakfast cereals. Sodium dihydrogen phosphate is used as a laxative, in pH adjustment, for treating surfaces before painting. Potassium phosphate is used to absorb H_2S, to control stability of latex. Potassium hydrogen phosphate is used as a buffer. Potassium dihydrogen phosphate is a piezoelectric, and a fertiliser. Ammonium phosphates (including hydrogen phosphates) are used as fertilisers, nutrients, flame retardants. Calcium phosphates are used in food and as fertilisers. Their other varieties are used as baking powder, toothpastes (except when fluoride is used), stock feeds, mineral supplements, etc. The use of calcium phosphates as fertilisers started from around 1830 when Liebig found that acidified bones act as good fertilisers. The world production of rock phosphate increased from around 500 tonnes in 1847 to 500 Ktonnes in 1880 to 150 Mtonnes in 1998, mainly to feed a growing world population.

We have not touched upon cosmetics and such other fast moving consumer goods (FMCG) items, which are also various chemical products, and demands for which has been on the rise. But more of that later.

Before we take up the historical development of chemical industries since 1900, we have to keep in mind the inequalities that exist between the producers and the consumers, even among different categories or classes of consumers. For example, towards the end of 19th Century (1880), coal replaced wood as the worlds main supplier of energy. Wood now accounts for only about 2% of energy supply of the world. Again, coal itself was superseded in 1960 by oil. Coal now accounts for about 30% of total energy of the world (vis-a-vis oil, which supplies about 33% of the latter, vide International Energy Agency data). Nuclear power did not exist before 1950, but now accounts for about 16% of world's power. This would not mean that in rural West Bengal or Karnataka, 30% of the households use coal, and about 16% use nuclear power. While nuclear power use is rather restricted in India, one would find wood as being a major energy source in such rural households. The percentage would be more in sub-Saharan Africa, or among indigenous population in Central or South America. However, nuclear power meets about 70% of electricity demands in France, including in several rural areas. Consumption of chemicals thus differ much between nations, and even between regions inside a nation, depending on availability of monetary resources over and above satisfaction of basic human needs.

Our discussion of the period from mid-19th Century till date, especially in relation to chemical industry, can be carried out on two different aspects of it viz. technological (and scientific), and economic, the latter side including all facets of trade and commerce as well. Let us deal with the scientific and technological aspect first. Scientific and technological changes related to chemical industry during 1850-2012 may be broadly classified into three groups viz. making natural compounds artificially, improving upon older / existing methods of making chemicals, and creating completely artificial molecules. The Haber-Bosch process and synthetic indigo are examples of the first type, whereas Solvay process of making soda is of the second kind. Perkin's synthesis of dye, or making of polymers such as Bakelite (and many other) plastics are examples of the third category.

In 1850, Great Britain was the biggest economic and political power in the world, and the largest producer of chemicals. In late 1860s, 304 Ktonnes of soda and 590 Ktonnes of sulphuric acid was produced in Britain, vis-a-vis 33 Ktonnes of soda and 43 Ktonnes of H_2SO_4. USA produced only 93.7 Ktonnes of sulphuric acid in 1970, and imported most of soda from Europe. But German and US industries grew much faster than their British counterparts. After the first decade of the 20th Century, Germany was producing 0.5 Mtonnes of soda (comparable to that in Britain) and 1.6 Mtonnes of sulphuric acid (350 Ktonnes more than in Britain). The USA was producing 2.2 Mtonnes of sulphuric acid, the largest in the world, by 1914. Even though synthetic dye was first produced in Britain, by 1914 Germany was producing nearly 28 times as much dyestuff. Even Switzerland was producing more than double the amount of dye produced in Britain. By this time, Germany was controlling 85% of the dye industry, most of the new pharmaceuticals, and in effect, about 40% of the chemical industry of the world. It is interesting that for most of the British chemical industry, Englishmen had to rely on the knowledge and expertise of French chemists, France could never become a major player in the world in this area. Some experts have suggested the socio-political developments in England and France were responsible for the difference between these two countries. While education and research in England was traditionally in the hands of learned societies and private enterprise, in France, the economic blockade following the Revolution forced the government to control these two activities. Also, almost everything in France is based in Paris, not distributed as in England.

Germany was kind of intermediate between England and France, there being several centres of learning and industrial enterprise, although not as ubiquitous as in England. However, the perseverance of German research in organic chemicals paid off in the 20th Century. Japan, the only other country to become a part of world capitalism, was still in its infancy in the early 20th Century. Her contribution to the world's chemical trade was around 1% by 1914. The chemical industry in the USA was started by a few individuals. An important contributor was E. I. Du Pont de Nemours, who fled with his father to the US to escape the French Revolution in 1799, to set up the first du Pont factory (producing ammunition) in 1802 in Delaware. He was an assistant of Lavoisier. By 1951, the USA was producing 43% of the world's chemicals, followed by Britain (9%), Germany (6%), France and Japan (4% each). Half a century later, world's production had increased about 10 times, the share of the US has declined to 28%, that of Britain only 3%, and those of Germany and France had remained at 6% and 4% (i.e., in their 1951 levels), but the share of Japan had increased to 13%. Germany remains the second largest chemical exporter after the USA in the first decade of the 21st Century.

One should not forget that A. W. Von Hoffman, an assistant of Justus Liebig, was recruited from Germany to Britain in 1845 to lead the newly formed Royal College of Chemistry. Liebig was a student of J. L. Gay-Lussac, who was a student of Berthollet, who in turn was trained by Lavoisier himself. Leibig started his teaching and research in the 3rd decade of the 19th Century in Germany. Hoffman, a leading chemist of his day, had to return to Germany as the British chemical industry was not prepared to invest in R&D at that time. However, Perkin, one of Hoffman's students in Britain, had synthesised the first artificial dye in 1856, which was to initiate the dye industry in Britain. In Germany, there was more interaction between industry and academia. Thus, the early exploration of individuals (entrepreneurs) in mid to late 18th Century gave way to consolidation and exploration about hundred years later. We must remember that Adam Smith's famous book on economics was published in 1776. The picture changed again half a century later, during and after the First World War.

The USA, deprived of European imports, especially of dyes etc., started to build its own organic chemical industry. It is not a coincidence that the most important British and German chemical companies, Imperial Chemical industries and IG Farben, were formed in 1926 and 1925 respectively. In the USA, there was competition and consolidation among companies such as du Pont, Union Carbide, Allied Chemical and American Cyanamid.

While the European industries were largely affected by the Second World War, those in the USA were not. The soldiers returned home to educate themselves and get jobs. The Depression years were over. The petrochemical industry in the USA developed quickly, based on demand for automobiles and allied petroleum products. An abundant supply of native oil and gas reserves helped. By 1950s, about 50% of production of organic chemicals in the USA was from natural oil and gas. A decade later, the ratio was nearly 90%. Another decade later, i.e., by the 1970s, European countries especially Britain and Germany were able to compete with the USA in terms of chemical output. Japan was the last major power to enter the world chemical market, around this time. Previously, its industry served domestic demands only. However, in around 1969-70 came the oil crisis, and the major players had to restructure their chemical industries to tackle this new challenge. Polymer products multiplied tremendously. Pharmaceuticals claimed an increasing fraction of chemical products in the market. Fast moving consumer goods (FMCG) articles also started their foray in the market from around 1970s and 1980s. Right now, polymers constitute about 33% of the total chemical output, and are the largest segment of the latter. Bulk petrochemicals and intermediates constitute 30% of total chemicals. Life science products, drugs and health products of humans and animals, diagnostics, pesticides etc., also make up 30% of total chemicals. Derivatives and basic industrial chemicals, synthetic rubber and rubber products, resins, dyes and pigments, turpentine, surfactants, explosives, carbon black etc. make up about 20% of total chemical products. Inorganic chemicals, salts, chlorine, caustic soda, soda ash, acids, etc. constitute 12% of total chemicals. Fertilisers (ammonia and nitrates, phosphates and potassic chemicals) make up about 6% of total chemical products. Speciality chemicals and FMCG products are rapidly increasing segments, and include electronic materials, industrial gases, adhesives, sealants, coatings, cleaning chemicals, catalysts, soaps, detergents and cosmetics.

In terms of employment, in the European Union, chemical industry generates over 3 million jobs in about 6,000 companies, and accounts for over 2/3 of the entire trade surplus of EU. In the USA, chemical production per year is around 750 billion dollars, employing over one million persons. The European Union remains the largest chemical producer, followed by the US and Japan. However, emerging countries and regions such as China, India, Korea, the Middle Eastern and South East Asian countries, and Brazil are making rapid progress. With the latest trend of outsourcing in the developed nations, production processes are moving to less developed (and emerging) countries, where labour is cheaper. But everywhere, the emphasis is on cutting costs and finding alternate (more efficient and cheaper) pathways to the same products. Also, newer chemicals such as nanomaterials, biomaterials, nano-bio composites, materials with pre-designed properties etc. are appearing in the markets. But throughout the period, i.e., 1850 till date, research and innovation has played a major role in the industry. W. H. Carrother's making of the first synthetic fibre, nylon, in the 1930s in Du Pont and Winfield and Dickson's synthesis of polyester, the most important artificial fibre, in 1941 are probably the most significant works for the industry. There have been other such contributions with products, catalysts, processes etc. With increasing use of computers, design and theoretical work has also become important. This is especially true of drugs. About a century ago, there was no testing of drugs; production was simultaneous with its introduction in the market. Today, a putative drug has to undergo rigorous testing at several levels before it can be brought to the market. Even then, action of previously unknown side effects may force the drug to be withdrawn within decades of its introduction. Refecoxib and celecoxib are examples of non-stereoidal anti-inflammatory drugs which were designed over years, and had to be withdrawn following harmful effects on patients with cardiac problems.

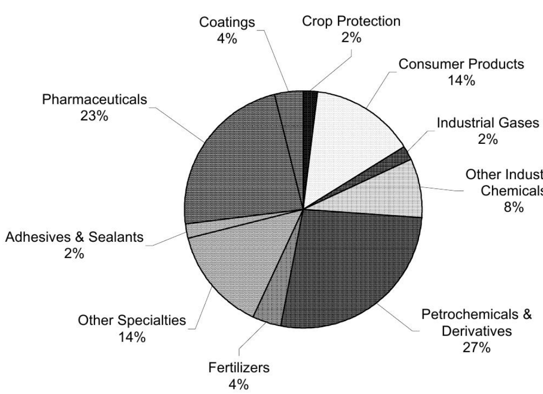

Figure 1: Global chemical production by segment, 2000. Source: American Chemical Council, Guide to the business of chemistry, 2001. Source: Ref [1].

Right from the early days, it was found that the HCl fumes polluted the atmosphere near the alkali plants. Towers were built which could absorb the fumes and the Alkali Act of 1861 was passed in Britain to make the towers compulsory for alkali plants. Also, much of the byproducts and solvents were often thrown unprocessed into rivers and ponds nearby, causing much environmental hazard. These had to be tackled and proper laws enacted. It was the constant investment in R&D that kept BASF, ICI and such companies as market leaders for over a century. Environmental degradation, however, continued, notable among them being the 1976 dioxin leak in Italy, the Love Canal incident in the USA in 1980, the Bhopal gas disaster from a Union Carbide plant in 1984, and two years later, fire in a Sandoz plant in Switzerland (1986) causing pollution in Rhine water.

The current picture can be better understood from the following figures. Fig. 1 shows global chemical production segmentwise, by 2000. Table 1 shows the evolution of chemical industry between 1850 and 2000. The data are given wherever available. The striking features that immediately draw attention are (1) the near constancy of US and France in terms of contribution to global chemical industry, (2) the fall of Britain as a major player in this field, (3) the rise of Japan as a major player in the same period, and (4) the fall of Germany upto 1950 and near constant ratio of global chemical output since then. Please note that in 1913, these 5 countries together contributed 80% of the global chemicals, while in 2000, their total contribution is only 54%. In other words, contributions from China, India and other countries have become important in the new Millenium. This becomes clear in Table 2, which gives the data for chemical exports from 1899 till 2000. This shows the European Union as the largest chemical exporter in the world by far, with US coming second by a large gap. It also shows that other countries, such as China, India, Brazil etc., not named in Table 2, have be-

Year	USA		Britain		Japan		Germany		France		World Total
1850	0.005										
1860	0.0047										
1870	0.0194										
1877							0.6	20%			3
1880	0.0386										
1890	0.0594										
1895							1				
1900	0.0626										
1905	0.0921										
1913	3.4	34%	1.1	11%	0.15	2%	2.4	24%	0.85	9%	10
1927	9.45	42%	2.3	10%	0.55	2%	3.6	16%	1.5	7%	22.5
1935	6.8	32%	1.95	9%	1.3	6%	3.7	18%	1.6	8%	21
1938	8.0	30%	2.3	9%	1.5	6%	5.9	22%	1.5	6%	26.9
1951	71.8	43%	14.7	9%	6.5	4%	9.7	6%	5.9	4%	166
1970	49.20	29%	7.60	4%	15.30	9%	13.60	8%	7.20	4%	171
1980	168.34	23%	31.77	4%	79.23	11%	59.29	8%	38.60	5%	719
1990	309.10	24%	44.70	4%	162.80	13%	100.50	8%	66.30	5%	1248
2000	460.00	28%	50.70	3%	218.40	13%	100.00	6%	73.00	4%	1669

Table 1: Production of chemicals in billion US$ and country shares (given as %). Source: Ref [1].

Exports from	1899	1913	1929	1937	1950	1959	1990	2000
United Kingdom	19.6	20.0	17.5	16.0	17.9	15.0	8.4	6.6
France	13.1	13.1	13.5	9.9	10.1	8.6	9.1	7.8
Germany [1]	35.0	40.2	30.9	31.6	10.4	20.2	17.7	12.1
Other Western Europe [2]	13.1	13.1	15.3	19.4	20.5	21.1	31.7	32.0
United States	14.2	11.2	18.1	16.9	34.6	27.4	13.2	14.1
Canada	0.4	0.9	2.5	2.9	5.2	4.4	1.8	1.6
Japan	0.4	1.0	1.8	3.0	0.8	3.1	5.4	6.1
Other	4.2	0.3	0.4	0.3	0.5	0.2	12.8	19.8
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Total in billion $ U.S.	0.26	0.59	1.04	0.98	2.17	5.48	309.2	566.0

Table 2: Chemical exports by country of origin from 1899 till 2000. Source: Ref [1].

come important globally. Fig. 2 analyses global chemical output by region, and by nature of countries themselves. The phenomenal rise of China can be clearly understood from Fig. 2. This is brought out more forcibly in Fig. 3 and Fig. 4. From Fig. 3, which shows global chemical production by region, the chemical production in Asia equals the total chemical production of Europe and America combined. NAFTA stands for North American Free Trade Association, including USA, Canada and a few other countries. Fig. 4, which compares the chemical production by regions between 2000 and 2010, clearly shows that emerging economies such as China far outpace the developed countries in chemical production in the second decade of the new millennium. Fig. 5 compares chemical production among countries in 2010, among both developed and less-developed countries. Here again, China emerges as the world leader, followed by USA. Japan and Germany are close together, behind the US. Other countries follow after them. It is interesting to note that Brazil and Korea come after Germany and Japan, ahead of India, Italy, and Taiwan. This also explains why

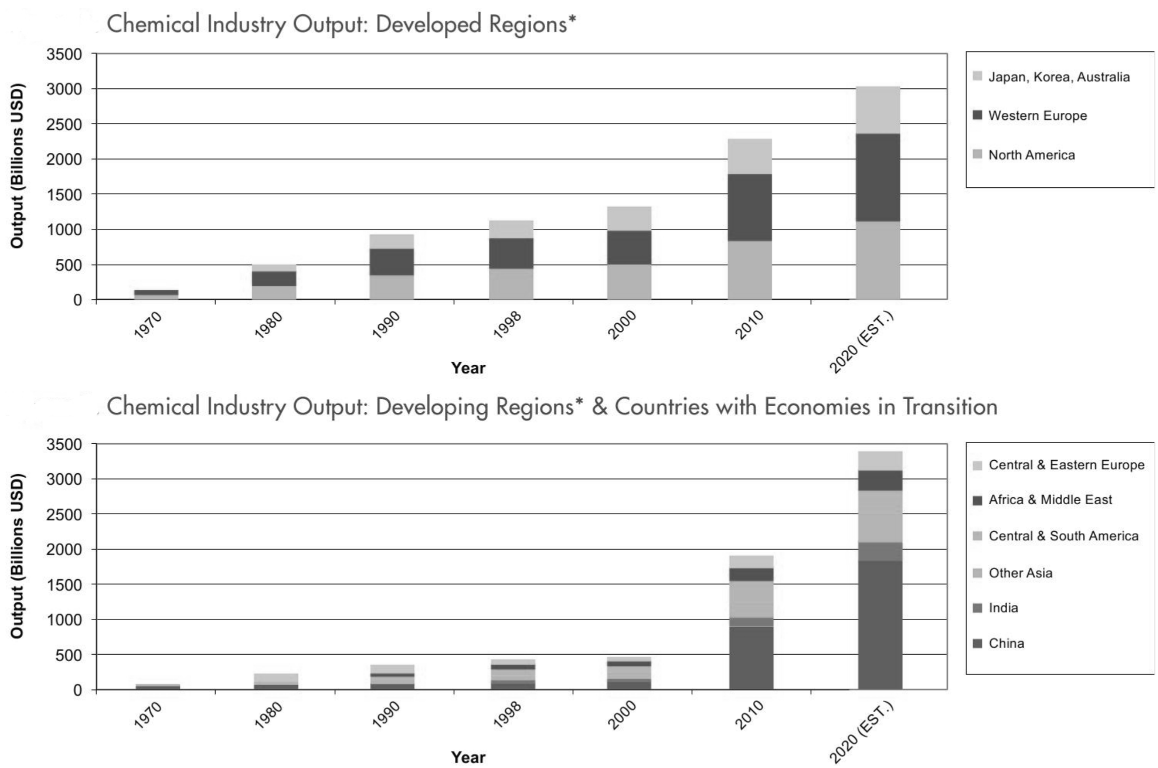

Figure 2: In each column on the top figure, the 3 units are for (a) Japan, Korea and Australia, (b) Western Europe and (c) North America, from top to bottom, in that order. Similarly, in the bottom figure, the different parts in each column signify data for (a) Centra & Eastern Europe, (b) Africa & Middle East, (c) Central & South America, (d) Other Asia, (e) India and (c) China, from top to bottom, in that order. Source: Ref [2].

the country-wise breakup of global chemical exports, shown in Table 2, is misleading as it does not indicate the production or sale of chemicals produced in a country, only chemical exports from it. In Asia, most of the chemicals produced within major chemical producers such as China or India are consumed within the country, demand being very high. Japan is the only exception, earning a lot from its exports.

Finally, one should be able to comment on future trends based on past history and current indicators. First, what will happen to traditional chemicals? We know that the older or heavy chemicals were superseded by newer ones such as pharmaceuticals or consumer products over the last couple of decades. Maybe nanomaterials or nanocomposites with biochemicals or other materials will become important in the coming decades. Already patents are being filed in this area at a tremendous pace.

Environmental issues are also important. More and more attention is being paid to environmental damages, as we are slowly becoming aware of exactly how much and how dangerously human industry has brought the environment to a "tipping point". Hence, more R&D efforts, and

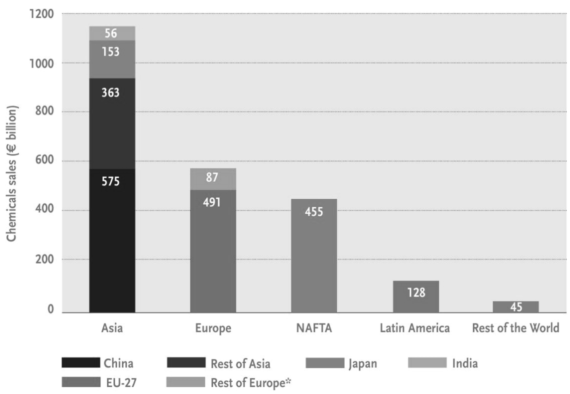

Figure 3: World chemical sales by region. In the column for Asia, the numbers are for China, Rest of Asia, Japan and India, serially from bottom upwards. In the column for Europe, it is EU-27 and Rest of Europe, from bottom to top. Source: Ref [4].

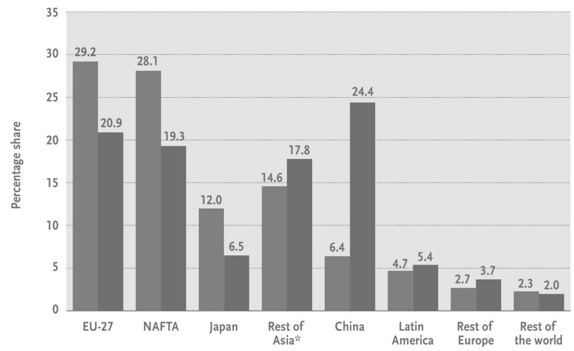

Figure 4: Comparison of world chemical sales between 2000 and 2010. For each pair of columns, the left one is for 2000 (total of Euro 1437 billion), and the right one is for 2010 (total Euro 2353 billion). Source: Ref [4].

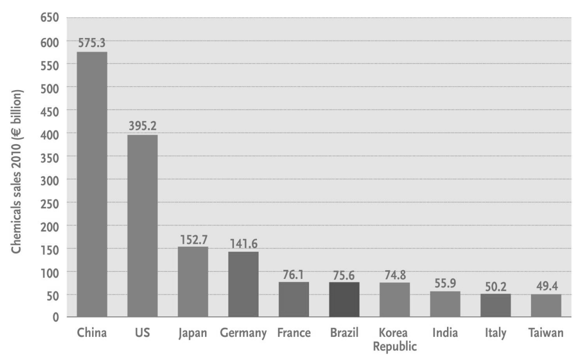

Figure 5: The top 10 chemical producing countries in 2010. Source: Ref [4].

more money, is expected to be spent on this aspect across the various chemical production units. Also, there is an interesting face-off between the economy of scale and tendency to miniaturise in chemical industry today. Attempts are being made, through outsourcing and R&D efforts, to reduce the number of steps in a chemical plant. At the same time, China has shown how large-scale production by cheap labour can catapult a country quickly into a position of global leadership. Increasing complexity of global socio-political scenario, combined with greater environmental disturbances, widespread water scarcity in large parts of Africa, Asia and Latin America, may make any long term prediction about the trends in chemical industry very difficult. □

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