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Review

Supercritical Fluids and Applications – A Patent Review

The view on the patent landscape for the application of supercritical fluids shows that the field is growing even stronger then 10 years ago. This proves the high attraction power even after 25 years of global development. Regional and branches statistics are shown. The number of independent patents filed in the area has reached 8600, showing that the use of specialized databanks is recommendable in order to keep the overview over the whole technology area.

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1 Introduction

Congress information, literature search, and patent surveys are common ways to evaluate the state of technology and to collect data for a future vision. If patents are available in structured databanks, a statistical evaluation might be useful for forecasting economies or research politics. A drawback is the long publication time for the majority of patents (see Fig. 1). Patents published within six months after priority date (international applications) are by far in the minority and regionally not representative, so that patent statistics based on them are of limited validity when applied to future trend evaluation. But, of course, the past and present situation can be reflected very efficiently by using the relatively large number of patents filed at present in the field of supercritical fluids.

Statistically evaluating the time between first priority date, application for a patent and appearance of a patent application in a public database leads to the result that availability of knowledge from patents takes in average two years in total, a time delay maybe too long for achieving a future vision.

Today, patent data are nearly comprehensively available and retrievable from public internet sources like the US Patent Office [1], the European Patent Office [2], and the Deutsches Patent- und Markenamt [3]. Moreover, commercial patent databanks like Thomson on STN (ex Derwent databases) [4] can increase the yield especially of patents coming from less open countries.

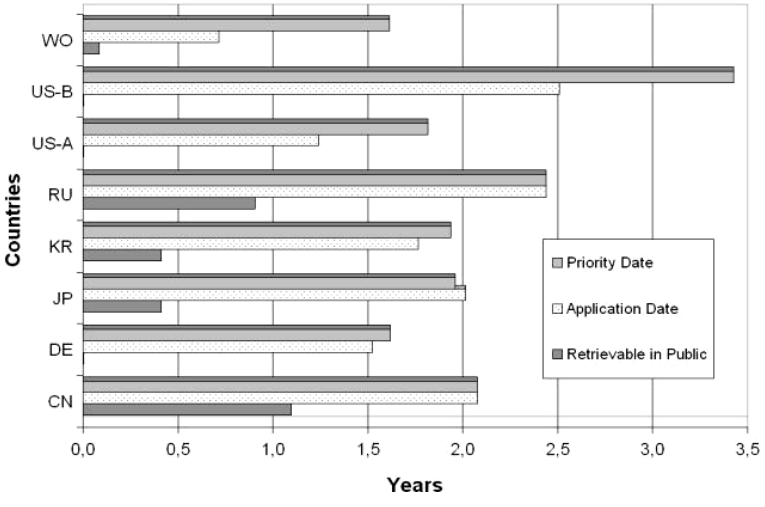

Figure 1. Time from first patent priority to public availability in Germany.

2 Material and Methods

The database material has been collected since 1992 with the aim of creating a representative bibliographic source of knowledge about supercritical fluid and compressed gas applications. Power plant and refrigeration technology are excluded; subcritical and supercritical water applications are included. The total database is contained in a Microsoft Excel table and includes about 10,000 records. It is commercially available.

As preparation for statistical evaluation, the material was filtered by relevance to the main topic. Generally, only one family member of a patent family was admitted to the evaluation. (This considerably reduces the number of patents as, in extreme cases, patent families consist of more then 100 family members.) Finally, to have an optimum access to the regional history of patents, all documents with international priority

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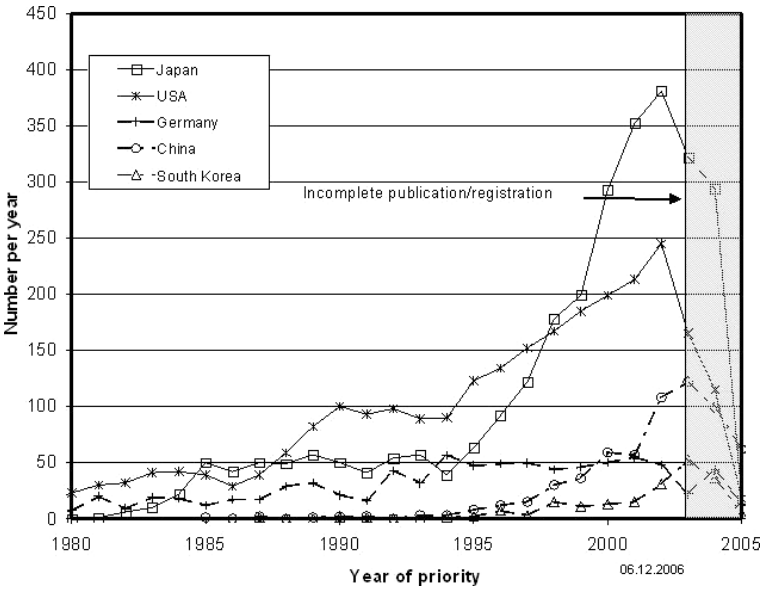


Figure 2. Regional number of supercritical fluids patent applications per year.

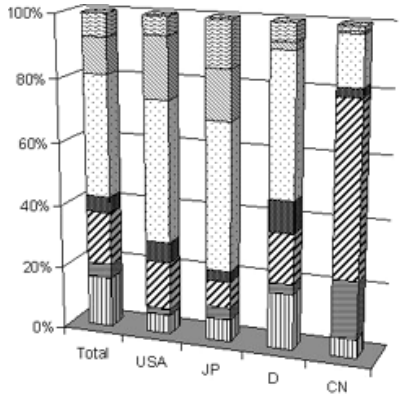
were nationalized. This operation is somewhat delicate but the mistakes occurring are expected to be of minor importance. The statistical differentiation has been made by evaluation of keywords which were set in a manner as consistent as possible.

3 Regional Characteristics

Tab. 1 shows the total number of patent applications of the most important countries. The numerical distribution of patents is reflecting well-known facts. The number of US documents is actually higher because of missing registration of part of the "laid-open" US documents. The amount of patents coming from Russia is surprisingly high. Most of them come from one source and cover a narrow field (number in brackets excluding those). The date of the last publication entry is only for orientation, for example, records from Asia appear in the public databases mentioned above four to six months after publication.

What is more informative is the time-dependent number of patent applications from different countries (see Fig. 2). The diagram area after 2003 (year of first priority) is shadowed because of incomplete coverage of patents. Going back to the 1980s, the US and Germany held a strong position in international comparison. But the steepest increase has occurred in Japan since 1995, leading to position 1 for new patent applications since 1998. In Germany, research activities have stagnated since 1995, not a promising sign for the future. In parallel to the speed of economical development China overtook Germany in 2000 regarding the number of patents filed per year with increasing tendency. A recent trend is that South Korea is accelerating and produces as much patents per year as Germany. What is interesting and worth being analyzed more deeply is the different slope of the curves based on Japanese and US patent applicants. A large quantity of new Japanese patent applications is dealing with hot water applications, another part focuses on the development of new (foamed) polymer materials.

In total, researchers show strong interest in supercritical fluids, there is no sign that the large increase over the last five years will end in a descending line. The only safe interpretation of the most recent time range is an increase in patents coming from China and South Korea.



	Total	USA	JP	D	CN
Environment	366	92	205	32	6
Semiconductors	566	301	221	13	3
Chemistry no SCWO	1918	694	654	254	62
Textiles	252	99	47	57	11
Pharma & Medicine	840	236	118	90	220
Diet (Food Suppl., Cholesterol...)	224	31	53	18	73
Food & Stimulants	794	94	100	100	24

Figure 3. Branch distribution in selected countries' patents.

Table 1. Main patent-applying countries for supercritical fluid applications (Sep. 27, 2006).

Country of origin	Number of applications	Last publication date
Japan	2794	July 13, 2006
USA	2636 (+approx. 200)	Aug. 31, 2006
Germany	860	Sep. 7, 2006
Russia	652 (62)	May 27, 2006
P.R. China	614	Feb. 22, 2006
South Korea	184	March 21, 2006
Great Britain	180	Aug. 10, 2006
France	171	July 13, 2006

For more knowledge about the regional characteristics it is useful to compare branch distribution in different countries. The result is shown in Fig. 3. Indeed, this figure gives a good impression of the preferences in the countries selected. So, in the US, the semiconductor branch is strongest, cosmetics are rather weakly represented. Japan is strongest in environmental applications (supercritical water) and has less interest in pharmacy and medicine. Germany focuses on textiles and food processing whereas very few semiconductor activities have been published. Finally, China's preferences are on health sciences, medicinal plant extraction and the processing of dietary supplements. To analyze the absolute strength of the different branches, it is necessary to read the absolute figures below the diagram.

4 Process Principles with Supercritical Fluids

Supercritical fluids are mainly applied as carriers for mass transfer, reaction media and solvents/antisolvents. If water above 100 °C is added as an own process field and analytics as a technique using mass transfer properties but following own directions, an array of process principles can be constructed and compared. Fig. 4, using the same diagram adjustments as Fig. 2, shows the historical developments of extraction, impregnation, particle design, reaction, supercritical water and surface treatment as key criteria.

The widest application of supercritical fluids was and still is extraction, especially with carbon dioxide. Its development has been nearly steady since 1980 (needless to say that nowadays fewer food products rather then technical materials are to be extracted.) The steep increase, beginning in 2000, is mainly related to the above Russian patent series with O. I. Kvasenkov as the inventor and misleading in the interpretation of the general trend of the curve. Chemical reactions represent the second largest group also with longer tradition and steady behavior. The development since 2001 has been less positive than of most other groups. A cross analysis of the supercritical water curve, which has been steeper in slope since 1995, shows that this increase mostly occurred in Japan. Particle generation processes seem to keep a strong position at present. The field of surface treatment applications, starting in the 1980s with varnish application techniques has now expanded to sophisticated wafer treatment methods and application of dielectric layers. Impregnation is a comparably small field but has gained considerable interest since 1995. An important innovation was textile dyeing with supercritical carbon dioxide.

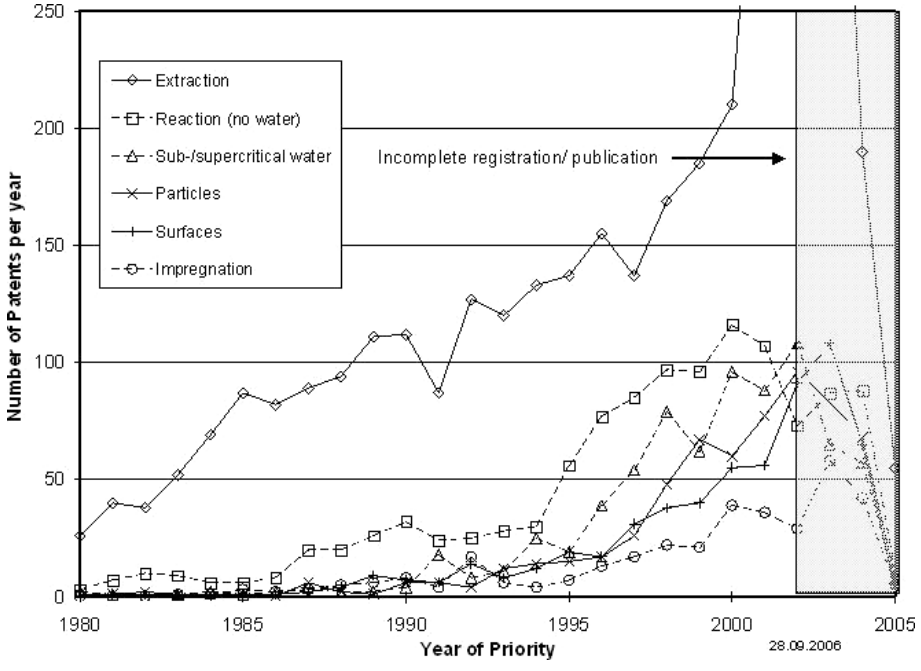


Figure 4. Historical development of process principles of supercritical patent applications (order equivalent to total number).

5 Companies and Institutions

Tab. 2 shows in alphabetical order the companies and research institutions with the highest number of patent applications in the field of supercritical fluids. The lists are self-explanatory except for some uncertainty about the correct definition of relationship of some Japanese companies and the statement that Russian research institutes are mostly involved in the group of about 500 patents in the field of fungi extract applications invented by Kvasenkov et al. Research strategy in Japan is traditionally strongly influenced by the activities of the Japanese Science & Technology Agency. In Japan, the business field for SCWO techniques seems to be strongly contested, which is reflected by the

Table 2. Most active companies and research institutions in supercritical patent activities (Jan. 2006).

Companies Name	Country	No. of patents
BASF AG	D	126
Degussa AG (SKW Trostberg AG)	D	65
Du Pont de Nemours Comp	USA	64
Exxon Mobil Oil	USA	96
General Atomics Inc.	JP	58
Hitachi Ltd.	JP	56
Ishikawajima Harima Heavy Ind Co Ltd.	JP	50
Japan Organo Co Ltd.	JP	109
Kobe Steel Ltd.	JP	72
Komatsu Ltd.	JP	66
Kurita Water Ind Ltd.	JP	65
Matsushita Electric Ind Co Ltd.	JP	71
Mitsubishi Heavy Ind Ltd.	JP	80
Mitsubishi Materials Corp	JP	47
Shell Oil Comp.	GB	52
Sumitomo Chemical Co	JP	60
Toshiba Corp.	JP	47
Toyota Motor Corp.	JP	66
Union Carbide Chem Plastics Tech Corp.	USA	55
(Public) Research institutions		
Battelle Memorial Inst.	USA	24
Canning Vegetables Drying Ind Res Inst.	RU	16
Comm Energie Atomique CEA	F	15
Deutsches Textilforschungszentrum Nordwest	D	13
Forschungszentrum Karlsruhe GmbH	D	19
Fraunhofer Ges Angew Forschung FhG	D	20
Idaho Res Found Inc.	USA	13
Inst Francais Petrole	F	21
Krasnodar Sci Tech Inst for Storage and Processing of Agricultural Products - Duktsii Krasnod Nii Khranenija I Pererabotki Sel SK	RU	38
Massachusetts Inst Tech MIT	USA	18
Nat Inst Adv Ind Sci Tech METI; Japan Sci Tech Agency; Agency Ind Sci Tech	JP	137
North Kaukasus local Sci Tech Inst for Horticulture and Viniculture – Sev Kavkazskij Zonal Nyj Ni S; Kij Inst Sadovodstva I Vinogra	RU	20
Russian Sci Tech Inst Biological Plant Protection – Vrnii Biolog Zashchity Rasten	RU	75
Shanxi Coal Chem Inst.	CN	28
Studiengesellschaft Kohle	D	30
Univ California	USA	45
Univ Kuban	RU	42
Univ North Carolina	USA	53
US governmental departments	USA	65

high number of patent applications from companies like Japan Organo Co. and Kurita Water Ind.

Of course, the absolute numbers of the list own some uncertainty, because many company names have changed in 25 years and the merger of companies has not been easily visible in every case.

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