



Green chemistry in Italy and Spain (1999–2019): Research policy lessons

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ABSTRACT

The study of green chemistry uptake in Italy and in Spain in its first two decades (1999–2019) offers numerous research policy lessons to research policy makers and chemical industry managers based in other countries. Both academic communities showed immediate interest in the new approach to chemistry productions based on the concepts of pollution and accident prevention, hazard elimination, and design for degradation. Spain's academic community acted in an organized manner and was able to attract tens of students to its master and doctoral international programs. Revealing differences exist also in the industrial uptake of sustainable chemistry and in research achievements.

1. Introduction

Green chemistry, namely “the use of chemistry techniques and methodologies that reduce or eliminate the use or generation of feedstocks, products, by-products, solvents, reagents, etc., that are hazardous to human health or the environment” (Anastas and Williamson, 1996) originated in the early 1990s at the Office of Pollution Prevention and Toxics and Industrial Chemistry Branch of the Environmental Protection Agency of the United States of America. The term “green chemistry” had been coined by Clive Cathcart in a journal article published in 1990, (Cathcart, 1990) though he will never be recognized in this respect by dominant advocates of green chemistry.

As shown by Linthorst, who identified the drivers behind the growth and evolution of green chemistry field in the USA, Great Britain and the Netherlands, a major driver behind the growth of green chemistry lies in the fact that “green chemistry” is an umbrella term with its own rhetorical force (and epistemic value) originating at the cutting edge of science and society (Linthorst, 2023). In the early 1990s Anastas did not use the term “green chemistry”, but rather used “benign by design chemistry” (Linthorst, 2023). This changed with a political action: the launch in the USA of the Presidential Green Chemistry Challenge Awards, that was announced in 1995 and became effective in 1996 in order to improve the public image of chemistry.

Eventually, following a period of modest increase in scholarly interest between 1993 and 1998, research in the field started to grow

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at substantial rate in 1999, when the Royal Society of Chemistry publishing branch (RSC Publishing) launched the new journal *Green Chemistry* (Linthorst, 2010). In year 2000 the journal published 70 articles. In 2016 it published 627 studies (Krishnan and Baskaran, 2018).

Beyond the aforementioned drivers behind the growth and evolution of the green chemistry in the USA, Great Britain and the Netherlands, (Linthorst, 2023) other studies have described the uptake of green chemistry in Brazil (Corrêa et al., 2013), India (Yadav, 2006; Veleva et al., 2018) and Russia (Tarasova et al., 2014; Lokteva, 2018). No studies, to the best of our knowledge, have been published on green chemistry uptake in Spain and Italy, even though researchers based in the two Mediterranean countries were (and are) amid the most prolific and pioneering contributors to the field. For instance, the book with the presentations given at the 1994 environmentally benign by design chemistry Symposium during the 208th national meeting of the American Chemical Society (ACS)”, included 5 out of 17 chapters written by Italian researchers (Chapters 3, 5, 6, 7 and 8). (Anastas and Williamson, 1996).

In chapter 3, Petrini and co-workers described the new EniChem process for the production of cyclohexanone oxime, a chemical intermediate for Nylon 6, from cyclohexanone, ammonia, and hydrogen peroxide mediated by Ti-containing silicalite (Petrini et al., 1996). The same catalyst was also successfully employed for the epoxidation of olefins by hydrogen peroxide, resulting in a process that is much more environmentally acceptable than the conventional method (Clerici and Ingallina, 1996). Researchers from the same company also described the synthesis of dimethyl carbonate, a non-toxic solvent and a versatile and environmentally innocuous intermediate, by oxidative carbonylation of methanol mediated by CuCl under relatively mild conditions (Rivetti et al., 1996).

These examples show that in the early 1990s the petrochemical industry in Italy, aware of the financial and environmental benefits of green chemistry, was actively engaged in reshaping chemical productions based on the key concepts of pollution prevention and material conversion efficiency. Similarly, the chemistry community in Spain acted quickly. In late 2002, five Spain's academics (Ramón Mestres, Avelino Corma, Félix Sánchez, Carles Estévez and José Antonio Mayoral) meeting at the Gordon Conference on Green Chemistry held in Oxford in September agreed on the idea to create a national Sustainable Chemistry Network (Mayoral, 2005). The Red Española de Química Sostenible (REDQS) is formally established as association in 2004. Four years before in Italy the interuniversity Italian National Consortium, Chemistry for the Environment (INCA) established in 1993 was funded by the European Community to organize in Venice the first Summer School on Green Chemistry as a three-year program (1998-1999-2000). (Tundo, 2000).

The study of green chemistry uptake in Italy and in Spain in research, education and industry during its first two decades (1999–2019) offers numerous research policy lessons to research policy makers and chemical industry managers based in other countries.

2. Results and discussion

2.1. Research

Table 1 shows the number of research articles and reviews (written in English) in the fields of green chemistry and sustainable chemistry published by researchers based in the top ten countries between 1999 and 2019 indexed by a large scientific database (Scopus). (Scopus, 2023).

Spain ranks 7th and Italy 9th in terms of scientific productivity. Out of 16,285 and research articles and reviews published between 1999 and 2019 in journals indexed by the Scopus database with the terms “green chemistry” (14,769) and “sustainable chemistry” (1516), researchers based in Spain authored 717 studies, and those based in Italy 664 (Scopus, 2023).

Table 2 and Table 3 show the first ten authors ranked by articles and reviews published in the two decades between 1999 and 2019 for Spain and Italy, respectively.

Besides Cordoba and Oviedo, the uptake of green chemistry research in Spain was particularly significant in Valencia and Alicante, with a remarkable presence of Spain's National Research Council (CSIC).

Pointing to the relevance of new education in green chemistry invoked since the early days of green chemistry, amid the most frequently journals used by researchers to publish their studies *The Journal of Chemical Education* ranked fourth after *Tetrahedron Letters*, *ChemSusChem* and *Green Chemistry*.

In Italy, the two most prolific authors are based at the universities of Pisa and Perugia, respectively. Alongside Italy's Research

Table 1

Number of research articles and reviews in the fields of green and sustainable chemistry published by researchers in the top ten countries between 1999 and 2019 (Source: Scopus, 2023).

Rank	Country	Number of studies published (green chemistry)	Number of studies published (sustainable chemistry)	Number of studies published (total)
1	India	2832	118	2950
2	China	2447	298	2745
3	United States of America	1967	223	2190
4	Iran	1323	34	1357
5	Germany	555	210	765
6	France	621	135	756
7	Spain	635	82	717
8	Great Britain	582	98	680
9	Italy	570	94	664
10	Brazil	576	33	609

Table 2

Spain's top ten scholars, and their affiliation, in green chemistry and sustainable chemistry by number of research articles and reviews published between 1999 and 2019 (Source: [Scopus, 2023](#)).

Name	Affiliation	No. of studies published
Luque, Rafael	University of Cordoba	34
García-Álvarez, Joaquín	University of Oviedo	15
Alonso, Diego A.	University of Alicante	12
Garrigues, Sandra	CSIC, Valencia	12
Corma, Avelino	Polytechnical University of Valencia	11
García, Hermenegildo	CSIC, Valencia	11
Herrero, Miguel	CSIC, Madrid	11
Ibáñez, Elena	CSIC, Madrid	11
de la Guardia, Miguel	University of Valencia	10
Baeza, Alejandro	University of Alicante	9
Nájera, Carmen	University of Alicante	9
Luis, Santiago V.	Jaume I University	9

Table 3

Italy's top ten scholars, and their affiliation, in green chemistry and sustainable chemistry by number of research articles and reviews published between 1999 and 2019 (Source: [Scopus, 2023](#)).

Name	Affiliation	No. of studies published
Benelli, Giovanni	University of Pisa	26
Vaccaro, Luigi	University of Perugia	25
Cravotto, Giancarlo	University of Turin	19
Tundo, Pietro	University of Venice	15
Aricò, Fabio	University of Venice	13
Lanari, Daniela	University of Perugia	12
Pagliaro, Mario	CNR, Palermo	11
Albini, Angelo	University of Pavia	10
Ciriminna, Rosaria	CNR, Palermo	10
Nardi, Monica	University of Catanzaro	10
Procopio, Antonio	University of Catanzaro	10

Council (CNR), the universities of Perugia, Venice and Catanzaro each have two researchers in the ranking.

2.2. Education

Initially supported by European funds, in Italy the INCA consortium between 1998 and 2023 organized in Venice fifteen editions of the annual Summer School in Green Chemistry. Typically lasting one week (five days), the international school attracted participants from more than 20 nations. Testifying to its international standing, the 2023 edition of the School saw among others the lectures (in person and online) of Lehn, Anastas, Jessop, Grätzel, Barbante, Licence, Triantafyllidis, Reiser and Aricò ([IUPAC, 2023](#)).

Education devoted to green chemistry in Italy flourished also within university departments. Following the introduction of short courses within selected universities like those of Venice ([Università Cà Foscari Venezia, 2023](#)), Pavia ([Università di Parma, 2021](#)) and Parma ([Università di Parma, 2021](#)) introduced the subject “green chemistry”, typically consisting of 48 h of teaching to students with a background in organic chemistry, within the Chemistry three year bachelor program. Demand of chemists specializing in green chemistry, however, is rapidly expanding. Hence, universities based in northern Italy recently launched three-year bachelor programs in Green Chemistry, ([Università del Piemonte Orientale, 2023](#)) often involving in the course design large chemical companies operating plants in those regions ([Università di Modena e Reggio Emilia, 2022](#)).

The Italian Chemical Society's interdivisional Green Chemistry Group was created in 2006. The team organized the first “Green Chemistry-Sustainable Chemistry” workshop in 2013. The first edition was attended by 60 chemists and 30 (oral and poster) presentations ([Piccolo, 2013](#)). The last, held in 2023, included a more than twice higher number of presentations (38 oral and 28 poster) than those given at the workshop held ten years before ([Società Chimica Italiana, 2023](#)).

In Spain, as mentioned above, the academic system acted coherently already in 2003 when REDQS (that also included researchers and professionals from industry) launched the interuniversity PhD program at nine universities which was (and still is) coordinated by the Jaume I University ([de la Hoz Ayuso, 2009](#)).

Noting that at that time (2009), organic chemistry textbooks did not use or include the sustainable chemistry concepts, University of Castilla's Professor de la Hoz Ayuso described in detail how since 2003 the network organized the aforementioned program (“Programa de doctorado interuniversitario en química sostenible”) that was eventually transformed according to Spain legislation in a Master program in Sustainable chemistry granting the doctorate degree since the academic year 2009-10 ([de la Hoz Ayuso, 2009](#)).

The program had remarkable success (“extraordinariamente positivo”) ([Altava et al., 2013](#)) and the whole system benefited. After the first decade (2003–2013), Santiago Luis and co-workers at Jaume I University could report that the cooperative effort and a modular design were the key drivers by which students received advanced education in green chemistry offered by REDQS scholars ([Altava et al., 2013](#)). When reviewing developments in 2015, it was found that some 250 students from more than 10 different

countries had attended the program (Luis et al., 2015). Some 30% of the students originated from abroad (mainly Latin America, where in all countries except Brazil Spanish is the common language, but also from other European countries and North Africa). All students who graduated from the programs were subsequently hired at chemical companies, or at Spanish and foreign universities.

Noticeably, the main problem emerged during the first decade of the program was found to be the increasing bureaucratic burden for which “intractable amounts of administrative forms” (Luis et al., 2015) forced educators “to devote more time to those administrative tasks, in many cases, than to the improvement” (Luis et al., 2015) of the educational work.

The vibrant activities of the program, nonetheless, actively continue today. In May 2022, the first two-day Symposium of the program organized in Castellón de la Plana had 27 oral presentations, including 2 invited lectures, and 24 poster presentations (Universitat Jaume I, 2022). Reflecting the standing of the science discussed at the meeting, for example, the oral communication “Parts-per-million of ruthenium catalyze the selective isomerization of terminal alkenes” given by Sanz Navarro, had been published as research article in Nature Communications six days before the start of the meeting (Sanz-Navarro et al., 2022). In May 2023 the first International Workshop on Sustainable Chemistry was organized and held in Cartagena, whereas very recently (January 2024) a Specialized Group in Green Chemistry was created within the Spanish Chemical Society (Real Sociedad Española de Química, RSEQ).

2.3. Industry

As mentioned above, the number of contributions from Italy’s large chemical industry to the first Symposium on benign by design chemistry held in 1994, (Rivetti et al., 1996; Petrini et al., 1996; Clerici and Ingallina, 1996; Clerici et al., 1996) shows evidence that industry was aware of the economic and technical advantages of the green chemistry approach to chemical productions. The same is true for Spain’s chemical industry that, with more than 3000 companies and over €64 billion turnover in 2022, is Spain’s second largest exporter in the Spanish economy, behind the automobile industry.

Established in 2005, SusChem-España is the Spanish branch of SusChem, an industry-led association including the European chemical industry association in partnership with the Royal Society of Chemistry created in 2004 with financial support of the European Union to promote initiatives to “revitalise the European chemical industry”. It is enough to review its activities through the social network most frequently used by researchers (Twitter) to understand its vibrant activities (Twitter, 2023).

For example, on September 28, 2023, de Mier (chief executive at a company using molecular modeling and artificial intelligence for more effective R&D) presented the case studies of chemical companies aided by molecular modeling and data science in the uptake of greener production processes (de Mier (NextMol), 2023). Remarkably, the aforementioned molecular modeling and artificial intelligence company is a spin-off company from the Barcelona Supercomputing Centre.

Awareness of the relevance of green chemistry to chemical industry’s competitiveness is widespread in Spain. For instance, the company starting up in 2021 the first chemical plant to manufacture linear alkylbenzene (LAB, high and low 2-phenyl) in Puente Mayorga (Cadiz), has a web page describing how the new technology replacing the process using toxic and highly corrosive hydrogen fluoride with fixed-bed *Detal* solid catalyst, reduces the annual water consumption by up to 80,000 m³ and substantially lowers the consumption of natural gas and electricity (Cepsa, 2022). LAB is the precursor to linear alkylbenzene sulfonate (LAS), the world’s most widely used biodegradable surfactant in laundry detergents. Both the operational and capital expenditures of the heterogeneously catalyzed *Detal* process are substantially reduced, thereby enabling the economic and technical viability of the process (Shokri and Karimi, 2021).

Besides affording higher quality product, the new process allows to flexibly meet the highly varying annual market demand. As such, it provides a vivid example of the 2019 forecast for which, driven by global societal megatrends concerning the environment, health, and energy which permeate societies on a global scale, chemical productions of the near future will use waste-free heterogeneously catalyzed continuous processes able to follow the highly flexible market demand (Pagliaro, 2019).

Getting back to Italy, with over 2800 companies and 3300 plants, the country’s chemical industry ranks third in Europe (after those of Germany and France). The sector in 2021 had about 112,000 employees and generated €56.4 billion revenues (Federchimica, 2023). Showing evidence of accelerated innovation needs, in the 2011–2021 decade the number of R&D employees has grown by 73% reaching 8350 in 2021. In the same year, Italy-based chemical companies invested €677 million in R&D activities (Federchimica, 2023).

The main sustainability achievements of Italy’s chemical industry in the last three decades (1992–2022), stem from substantial process engineering improvements. Italy’s main chemical companies (173 firms with overall revenues of €35 billion) (Federchimica, 2023) take part in the Responsible Care environmental performance program. The outcomes have been substantial energy and material efficiency improvements, with dramatic reduction, for example, in the amounts of energy (–50% primary energy required in 2021 with respect to 1990) and water (–44.1% with respect to 2005) consumed by the industry (Federchimica, 2023).

Significant less successful, on the other hand, has been the uptake of green chemistry concepts and methodologies. For instance, according to the association of Italy’s chemical firms, sustainable chemistry should be preferred to green chemistry, because the word “green” would indicate “the industry that exclusively uses natural raw materials, and is contrasted to other productions”. (Federchimica, 2018).

Economically viable green chemistry processes, on the other hand, are necessary but not *per se* sufficient for successful biobased productions (Ciriminna et al., 2024).

This misunderstanding resembles a case from the Netherlands when in 1991 a special issue called “Groene Chemie” completely devoted to biomass was published in a Dutch chemical magazine. (See Chapter 4 in Linthorst, 2023) Similar misunderstanding often arises from insufficient knowledge of green chemistry history and conceptual foundations for which it happens to read in a 2022 publication that “the term green chemistry was invented by Paul Anastas at Berkeley in 1991”. (Della Volpe, 2022).

Dr Anastas however, was not an academic research chemist but a policy chemist employed at the EPA first (between 1989 and

1995) at the Industrial Chemistry Branch and subsequently (between 1995 and 1999) as director of the new Green Chemistry Program. He earned his PhD in chemistry from Brandeis University and actually never worked in Berkeley (California). Dr Warner, with whom he co-authored in 1998 the 12 principles of green chemistry, (Anastas and Warner, 1998) was an industrial research chemist who in 1996 had returned to academia joining the University of Massachusetts (Warner, 2023).

From accident prevention and design for degradation, through real-time process monitoring and energy efficiency, many of the principles of green chemistry (Fig. 1) clearly reflect the industrial expertise of their proponents.

In brief, green chemistry has different (intellectual and contextual) origins (Linthorst, 2010). Among those roots stand industry and the industry-government interface of environmental protection agencies. In addition, the negative public image of chemistry has also been an important origin of green chemistry.

The main green chemistry principles that originate in academia are catalysis and atom economy, but even the latter concept owes much to Sheldon who worked as industrial chemist for more than two decades, first (between 1969 and 1979) as laboratory technician at a large petrochemical company and subsequently (between 1980 and 1990) at a large fine chemicals company where he eventually became R&D director prior to join Delft's Polytechnic (Professor Roger Sheldon, 2023).

In Italy too, as testified by the four (out of 17) chapters of the first international Symposium devoted to green chemistry in 1994, (Anastas and Williamson, 1996) green chemistry chiefly originated in industry. The subsequent wave of privatizations, plant closures, mergers and acquisitions that deeply affected Italy's chemical industry in the 1990s, (Negri et al., 2007) were not supportive of green chemistry uptake. Eventually as mentioned above the main sustainability achievements of the Italian chemical industry stem from the chemical engineering approach to process optimization (Federchimica, 2023).

Things started to change during the (2004–2014) decade when chemical companies chiefly consisting of small and medium-sized enterprises emerging from the break-up of Montedison (an integrated, multinational chemical company with 150,000 employees) focused on the production and export of high added-value products in the fine chemical and specialty sectors, becoming true “pocket multinationals”. (Colombo, 2014).

Amid said companies, the first industrially significant change towards green chemistry occurred in the early 2020s when some of Italy's largest fine chemical companies supplying active pharmaceutical ingredients active started to use continuous flow chemistry reactors. One of them, which is one of the largest in Europe, in 2019–2021 invested in new pilot-scale flow reactor systems to meet its customer production evaluation requirements “from R&D feasibility” through “mid-scale and commercial production”. (Sternberg, 2011).

Noticeably, this is in agreement with a 2016 forecast for which after the “technology push” phase (raising awareness, curiosity and learning) between 2008 and 2018, from 2018 industrialization of flow chemistry would have led to a “market pull” first in China and India, and then in Europe, North America and Japan (Pichon, 2016). According to Pichon, this industrialization phase will last until 2028, followed by a maturity phase in which the market share of flow vs. batch will reach and surpass the 30% threshold (Pichon, 2016).

3. Conclusions

In conclusion, four main lessons of direct relevance to research policy makers and chemical industry's managers emerge from the analysis of the uptake of green chemistry in Italy and in Spain in research, industry, and education.

First, the remarkable success of Spain's cooperative efforts to deploy a national program in advanced (postgraduate, master and doctoral) education going back to the early 2000s teaches that interuniversity cooperation and coordinated action to deploy modular (and not overlapping) educational curricula and courses is a key driver to organize advanced education of international standing.

Second, the fact that Spain was able to attract tens of master and doctoral students from foreign countries, including other European countries, shows evidence that a coordinated national effort on advanced, prolonged education on green chemistry can attract bright students from many countries, regardless of the “significant economic crisis suffered by Spain in the last few years” (Luis et al., 2015). Incidentally, a similar success of the brief education offered by Italy's INCA Summer school on green chemistry suggests that this is the case also for short educational initiatives.

Third, the exceptional achievements in research on green and sustainable chemistry of Spain's scholars show that coordinated and cooperative efforts are key drivers of successful research, too. Both Italy's and Spain's academic communities showed immediate interest in the new approach to chemistry productions based on the concept of pollution and health hazard prevention. Whereas Italy's researchers were amid the early proponents of said approach (Petri et al., 1996; Clerici and Ingallina, 1996; Rivetti et al., 1996), Spain's chemistry academic community acted in an organized manner and in two decades (1999–2019), its research community

Prevention	Atom economy	Less hazardous chemical syntheses	Designing safer chemicals
Safer solvents	Energy efficiency	Renewable feedstocks	Avoid derivatives
Catalysis	Design for degradation	Real-time analysis	Accident prevention via safer chemistry

Fig. 1. The 12 principles of green chemistry according to Anastas and Warner (1998). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

emerged amid those globally leading in this key area of chemistry research.

Fourth, the delayed uptake of green chemistry of Italy's chemical industry in favor of a process optimization approach chiefly relying on improved chemical engineering, suggests that a closer and organized interaction between universities and public research bodies is needed. In other words, said collaborations should no longer be based on the self-determination of scholars as it happens at Italy's Research Council (Pagliaro and Coccia, 2021).

Many ways exist, in conclusion, to promote said closer and organized interaction as well as to integrate the internal, non-structured form of R&D activities based on learning-by-doing at most Italy's chemical SMEs (Negri et al., 2007). One of the most effective involves the exchange of researchers between companies and research institutions. For instance, enabling completely new levels of process control and modeling, data-driven computational science allows to dramatically reduce the cost of switching from multi-step productions in batch, to digitally-controlled and nearly waste-free chemical productions under flow. In order to transfer these concepts and skills to undergraduate students, academic researchers and educators need to learn the practice of said innovative productions at the companies which already operate them.

Similarly, they should be aware that the COVID-19 actually acted as a "catalyst" for continuous manufacturing in the fine chemical industry, (Wiles, 2021) namely the industry that manufactures virtually all pharmaceutical ingredients, "specialty" and "agro" chemicals in the continuously stirred tank reactor typical of the industry.

The chemical industry is intrinsically risk averse, due to the large capital expenditure required to build a new conventional in batch manufacturing plant. However, thanks to significantly reduced capital and operating expenditures, continuous manufacturing in much smaller and modular plants relying on shorter, lower risk supply chains is emerging as the chemical production technology able to address supply challenges and meet local demand in Europe and North America from where most fine chemical productions were outsourced to India and China.

For example, France-based industrial researchers reported in 2020 a very efficient and nearly waste-free continuous manufacturing process of acetaminophen (paracetamol), in which the key step of the process is the continuous hydrogenation of *p*-nitrophenol over a new generation solid catalyst at very low load in three reactors of increasing capacity placed in series (Lecomte-Norrand and Membrat, 2021). Shortage of paracetamol affected both France and Germany during the COVID-19 health crisis.

"This mode of construction and the implementation of new technologies" said Lecomte-Norrand presenting in mid 2023 the continuous process for the production of acetaminophen, "is the only way to make the relocated production profitable" (Lecomte-Norrand, 2023). In other words, continuous manufacturing using heterogeneously (and homogeneously) catalyzed processes is emerging as the key technology enabling to re-shore the productions of APIs, (Ciriminna et al., 2021) ending the supply mode that dominated during the thirty years of the second globalization era (1991–2021) during which stock piles were used to manage demand and any supply chain disruption.

In the expanded education of chemistry and chemical engineering faculty willing to contribute through applied research (and practice-oriented education) to innovate chemical productions based on newly developed green chemistry processes, these and related research policy and industrial economy aspects cannot be ignored any longer.

CRedit authorship contribution statement

Rosaria Ciriminna: Writing – review & editing, Project administration, Funding acquisition, Formal analysis, Conceptualization. **Matteo Formenti:** Validation, Investigation, Data curation. **Cristina Della Pina:** Writing – review & editing, Data curation, Conceptualization. **Rafael Luque:** Writing – review & editing, Supervision, Methodology, Conceptualization. **Mario Pagliaro:** Writing – original draft, Supervision, Formal analysis, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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