Vanillin: Synthetic Flavoring from Spent Sulfite Liquor[1]

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Abstract

Separation of the lignin component of wood from the cellulose presents an opportunity to access various interesting products from the lignin fragments. The lignin represents availability of a sizable renewable resource. Vanillin, or 3-methoxy-4-hydroxybenzaldehyde, is one of a series of related substituted aromatic flavor constituents, and represents one of the potentially profitable possibilities. Vanillin production from the lignin-containing waste liquor obtained from acid sulfite pulping of wood began in North America in the mid 1930's. By 1981 one plant at Thorold, Ontario produced 60% of the contemporary world supply of vanillin. The process also simultaneously decreased the organic loading of the aqueous waste streams of the pulping process. Today, however, whilst vanillin production from lignin is still practiced in Norway and a few other areas, all North American facilities using this process have closed, primarily for environmental reasons. New North American vanillin plants use petrochemical raw materials. An innovation is needed to help overcome the environmental problems of this process before vanillin production from lignin is likely to resume here. Current interest in the promotion of chemicals production from renewable raw materials reinforces the incentive to do this.

Keywords

Organic Chemistry
Public Understanding/Appreciation
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Industrial Chemistry
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Supplementary Materials

No supplementary material available.

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Vanillin is the chief constituent of natural vanilla flavoring, used in foods for centuries. Cortez is said to have been served a chocolate drink flavored with vanilla by the Aztecs in about 1520. He brought the knowledge of both chocolate and vanilla back to Spain and Europe, where they rapidly became popular. Use of natural and synthetic vanilla as flavorings has continued to grow since then; by 1850 their household use was so common that they inspired the quotation "Ah, you flavor everything; you are the vanille of society" (*1*). Today, vanillin, as vanilla flavor, and methyl salicylate, as wintergreen flavor, are the largest-volume synthetic food flavorings in common use.

Structurally vanillin, or 3-methoxy-4-hydroxybenzaldehyde (**3**) and methyl salicylate (**5**) are members of a group of flavoring and essence compounds all with related structures (Fig. 1). Ethyl vanillin (**4**), the *meta*-ethoxy analog of vanillin, is also used commercially as a vanilla flavoring; it has about 3.5 times the flavor intensity of vanillin itself. It is intriguing to observe the minor structural differences among these materials and speculate on the factors responsible for the shift in flavor from the relatively mild to sweet varieties used in bakery goods and confectionery, such as almond and vanillin, to the more intensely flavored zingerone, the chief flavor component of the sweet or savory uses of ginger, to the 1000+ times more potent capsaicin, the principal "hot" flavor constituent of cayenne, jalapeño, and habañero peppers. Capsaicin is also the chief active ingredient in the oleoresin capsicum, used in pepper sprays and marketed at 2% strength for personal defensive use ($3^{1}/_{2}$–5% to discourage aggressive dogs, and 10% as a bear repellent [without guarantee]).

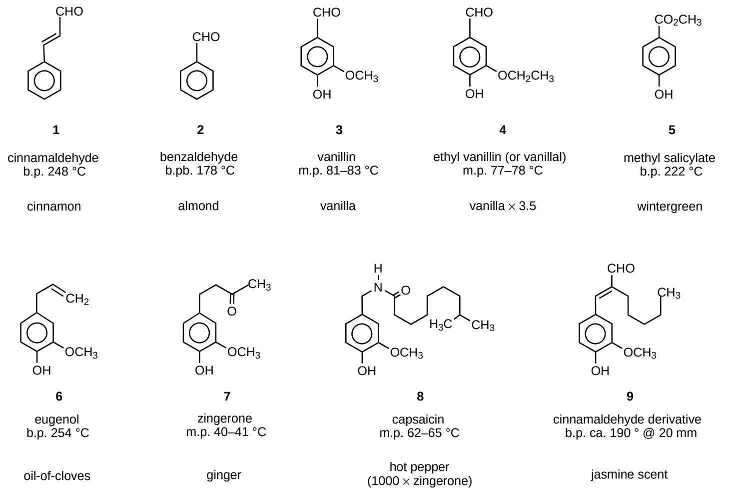
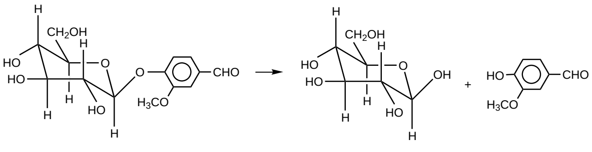


Figure 1. Structural relationships between a group of important flavor essences and a perfume ingredient. True jasmine scent from jasminal is less intense than from the derivative illustrated here and does not have the aromatic hydroxyl and methoxyl substituents.

Vanillin occurs widely in nature in trace amounts in the woody tissues of plants, as well as in commercial products such as tobaccos (*2–4*). The characteristic aroma of vanillin is very noticeable from the bark of the ponderosa pine (*Pinus ponderosa*). The highest natural concentrations, 1–3% and sometimes higher, are found in the properly cured pods of the "vanilla bean". Vanilla beans are harvested from species of the *Vanilla* orchid, a tropical climbing plant that derives all its sustenance from the air and rainfall. The vanillin in the green bean as picked is tied up as the glucoside, and hence does not have the telltale smell of vanillin at this stage. But after the proper maturation processes of drying and warmth causing "sweating", the vanillin glucoside, **10**, is enzymatically hydrolysed to glucose, **11**, and vanillin, **3** (eq 1).



(1)

10 **11** **3**

The bean, at this stage brown and somewhat shriveled, is now readily recognized by smell as a source of the popular vanillin flavor. Either the cured bean itself or its extract with warm aqueous ethanol (35% v/v) may be used to produce natural vanilla flavoring. Flavor contributions from the bean itself are obtained by direct extraction of the bean using the warm fluids used in baking or other cookery. However, the brown solution of natural vanilla as an extract in aqueous ethanol is a form more convenient to use for many purposes (Table 1).

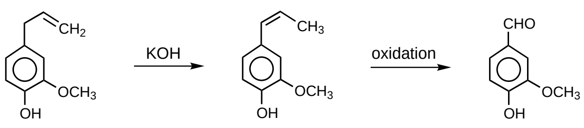
Table 1. Concentrations of Principal Aromatic Polar Compounds in Natural Vanilla Extract[a] (*5*)

Constituent	Concentration (mg/100 mL)
Vanillin	135–175
4-Hydroxybenzaldehyde	10–12
Vanillic acid	7–8.5
4-Hydroxybenzoic acid	1.5–3.3

[a] Natural vanilla extract is defined as containing the extractable matter of 13.35 oz of vanilla beans (having a maximum moisture content of 25% w/w) per U.S. gallon of 35% (v/v) ethanol in water (*5*).

Vanillin Isolation, Preparation

Gobley, in 1858, was the first to isolate and identify the vanillin constituent of the vanilla bean and to confirm that this was the chief flavor component (*6, 7*). The high prices, plus the vagaries of weather that affect the volume of vanilla beans produced each year, provided a strong stimulus for the preparation and marketing of synthetic vanillin as a supplement to natural sources. In 1874–75, less than 20 years from its initial isolation, synthetic vanillin prepared from eugenol, **12**, became available in France and the United States and sold for U.S. $176 per kilogram (*8*) (eq 2).

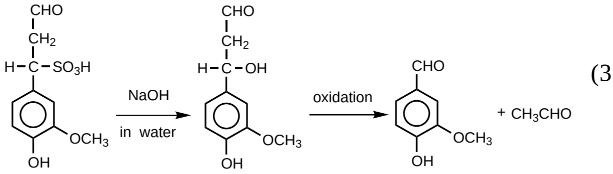


(2)

12 eugenol **13** isoeugenol **3** vanillin

With vanilla beans of only 1–3% by weight vanillin selling for US $5.50–8.00 per kilogram—that is, $180–800 per kg of vanillin content, this was still competitive. Eugenol from oil of cloves continued to be a starting material for synthetic vanillin production until at least the 1920s (*9*).

The first hints that it might be possible to produce vanillin from lignin-containing wastes came from an anonymous report in 1875 of a vanillin-type smell in spent acid sulfite pulping liquor, confirmed by Grafe on his pyrolysis of dried waste sulfite liquor (*10, 11*). This possibility was better established by the detailed research of Howard and others in the United States (*12*), and at McGill University by Tomlinson and Hibbert (*13, 14*). Howard patented methods to concentrate the required lignin fraction of the pulping waste, an important preliminary. The McGill group found that the yield of vanillin varied somewhat with the source of the liquor and with the degree of lignin sulfonation. They proved that up to 2.6 g/L of vanillin (up to 5.9% of the lignin content) could be recovered from waste sulfite liquor (eq 3). Freudenberg showed a little later that lignin-based vanillin yields as high as 10% using air or 20–30% using nitrobenzene as the oxidant were possible in the laboratory (*15*). The higher yields possible with nitrobenzene were commercially unattractive because of the need to deal with the co-produced nitrobenzene reduction products.



(3)

sulfonated lignin fragment **3** vanillin acetaldehyde

Commercial Vanillin from Lignin

Production-scale preparation of vanillin from the lignin of waste sulfite liquor began in the United States in 1936 as a joint venture of the Salvo Chemical Corp. and Marathon Paper Mills Co. of Wisconsin, using the technology developed by Howard (*16*). A year later Howard Smith Paper Mills Ltd. began the first Canadian production-scale plant at Cornwall, Ontario, based on the research work conducted at McGill (*17, 18*). Further studies by Ontario Pulp and Paper in the 1940s led to the construction of a second Canadian vanillin-from-lignin production unit on the scale of 227,000 kg per year at Thorold, Ontario in 1945. Integral with the vanillin operation of this plant was an initial fermentation step that could make use of the 3–5% ferment-

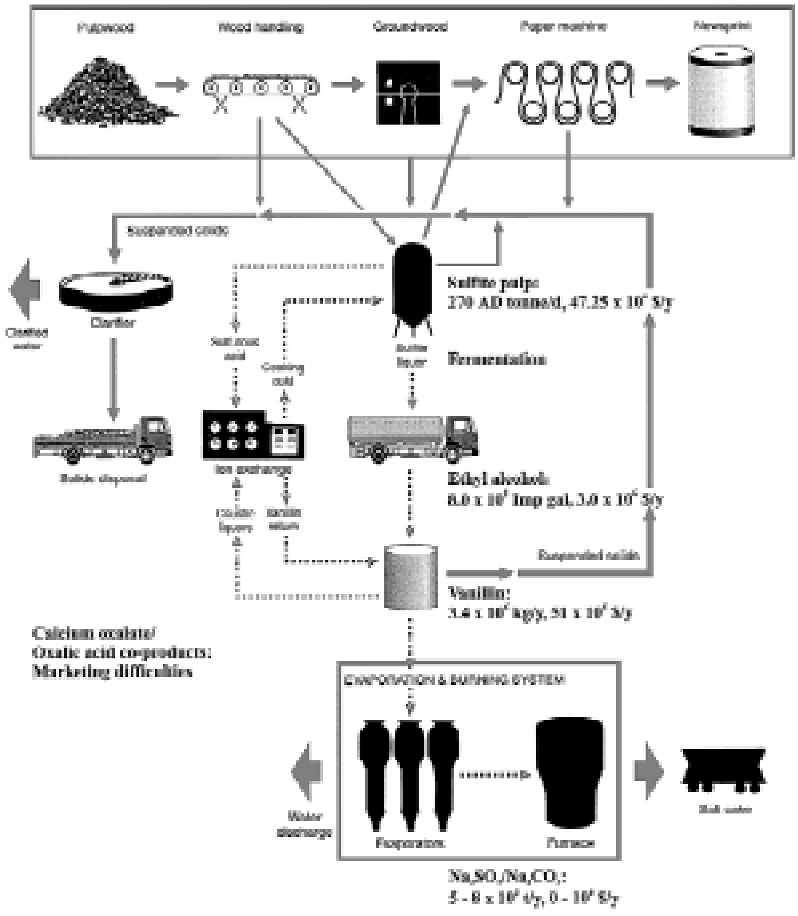


Figure 2. Integration of a fermentation plant, and vanillin preparation for spent liquor values from an acid sulfite pulp mill, as adapted from a company brochure. The annual production values given are estimated from production rates reported for Ontario Pulp and Paper at Thorold (*21, 22*), as follows:

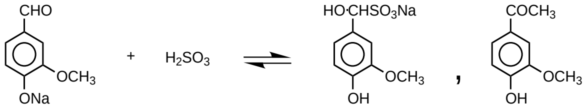
pulp, 270 air-dry tons per day × 350 d/yr × 500 Can $/ton = 47.25 × 10^6 $/yr

ethanol (96%), 8.0 × 10^5 Imp gal/yr × 3.75 Can $/Imp gal = 3.024 × 10^6 $/yr;

vanillin, 3.4 × 10^6 kg/yr × 15 Can $/kg = 51 × 10^6 Can $/yr;

saltcake, Na_2SO_4/ca. 30% Na_2CO_3, (5–8) × 10^5 ton/yr × 0–70 Can $/t = 0–$10^6$ Can $/yr.

able sugars commonly present in spent acid sulfite pulping liquors before vanillin production and recovery (Fig. 2). After making the "fermentation black liquor" alkaline and oxidation with air at 160–170 °C and 10–12 atm pressure, the oxidation product stream was extracted with toluene and then back-extracted with aqueous sodium hydroxide. The aqueous solution of crude sodium vanillate (**14**) obtained in this way was then purified via the carbonyl sulfite addition compound by addition of aqueous sulfur dioxide (eq 4). The soluble addition compound of vanillin (**15**) was thus readily separated from acetovanillone (**14**) and other insoluble phenolic impurities by filtration. To produce a food-grade product the vanillin was then reprecipitated from this aqueous solution by neutralization and vacuum-distilled, with a final purification by crystallization. Full quantitative details of an early version of this process have been published (*19*).



(4)

14 sodium vanillate   **15** sulfite addition compound   **16** acetovanillone

The vanillin production of Ontario Pulp and Paper became such a valuable component of their operations that the scale was gradually expanded to 3.4 million kilograms per year by 1981, sufficient to supply 60% of the then current world market. This also began to subtly affect the pulping component of their business.

The vanillin recoverable on the proper processing of waste sulfite liquor is produced from guaiacyl units (**18**) of the lignin (**17**), which is sulfonated and solubilized during the pulping of wood for the production of chemical pulps. When the raw wood used for pulping is coniferous in origin, the bulk of the appropriate building blocks in the lignin are guaiacyl, and the dominant aldehyde product on alkaline oxidation of the partially sulfonated lignin is vanillin (**3**) (Fig. 3). In contrast the appropriate building blocks in the lignin of deciduous woods comprise mostly syringyl units (**19**) with only a relatively small proportion of guaiacyl units. Consequently alkaline oxidation of the spent sulfite liquor from the pulping of deciduous woods gives mostly syringaldehyde and lower yields of vanillin. Realizing this, Ontario Pulp and Paper trucked coniferous wood from greater distances rather than use closer supplies of deciduous wood for pulp production, in order to keep their yields of vanillin from the waste liquor high. This represents a prime example of the feedstock of an industrial operation being influenced as much or more by a "waste stream" product as by the primary product, in this case the chemical pulp destined for use in newsprint production—a case of "the tail wagging the dog"!

The chemistry of vanillin recovery from lignin is an interesting reflection of the oxidation-stabilizing contributions of the hydroxyl and one or two methoxyl substituents for the two aromatic aldehydes, vanillin and syringaldehyde. While these aldehydes are slowly oxidized by air, without this substituent stabilization the recovery conditions used would lead to rapid oxidation of these products to the corresponding vanillic and syringic acids, **18** and **19**, R = carboxyl, of less value as flavor constituents.

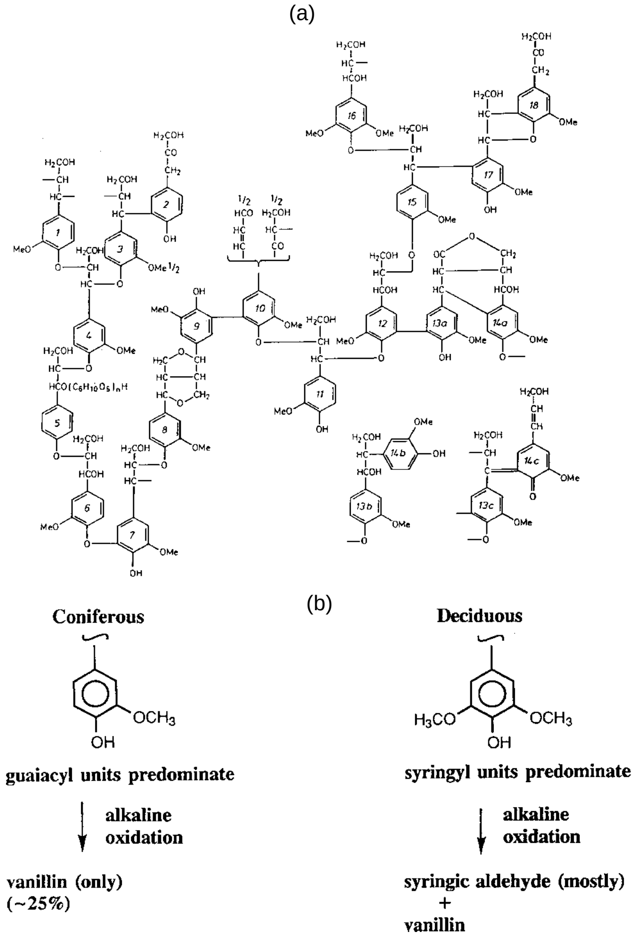


Figure 3. (a) Lignin model segment adapted from Hocking (*20*). (b) A generalization of the respective pathways to vanillin from a softwood (coniferous) lignin, and a mixture of syringaldehyde plus vanillin from a hardwood (deciduous) lignin.

Table 2. Trends for Natural Vanilla Beans and Synthetic Vanillin in U.S. Market

Year	Natural, as Beans[a]			Synthetic, as Vanillin[b]		
	Metric Tons	U.S. $/kg	Ref	Metric Tons	U.S. $/kg	Ref
1874	–	5.50	*8*	–	176	*8*
1913	363	–	*8*	0.025	–	*8*
1924	360	19.80	*8*	–	18	*8*
1934	360	7.70	*8*	–	6	*8*
1938	360	–	*8*	206	8.80	*8*
1951	–	–		453	6.60–9.00	*19*
1971	–	11.00–18.50	*24*	–	11	*25*
1980	–	88–101	*24*	–	11–12	*25*
1991	498	33.30	*24*	4500–5500	11–14	*25*
1992	437	27.60	*24*	4500–5500	11–14	*25*

[a] Of 1–3% vanillin content. Price is subject to wide fluctuations both month-to-month and from quality/source considerations (e.g., Madagascar, Tahiti, Java, Mexico, Indonesia). Prices quoted are intended only as representative.

[b] Major current world producers of vanillin and their estimated capacities in metric tons per year are: Rhône-Poulenc, 4500; EuroVanillin, 2300; Chinese producers, >454; Ube Industries (Japan), ca. 204; Wlocvavek Plant (Poland), ca. 50 (*25–27*).

Table 3. The Shift in Uses of Vanillin with Time[a]

Time	Use	Example
1960	Flavoring (~85%)	Beverages, 200 ppm
		Bakery products, 1900 ppm
		Ice cream, 3000 ppm
		Candy, 4000 ppm
	Masking fragrance, industrial products	Paint, to mask odors during drying, 500 ppm
1970 →	Chemical intermediate for syntheses (>50%)	Papaverine (treatment of heart problems)
		Hydrazones (2,4-D-like herbicides)
		Antifoam (lubricating oil additives)
		L-Dopa (Parkinson's disease treatment)
		L-Methyldopa (antihypertensive drug Aldomet)
		Trimethoprim (antibacterial agent)

[a] Note that vanilla beans and genuine vanilla extract remain almost exclusively in use as a flavoring because of cost.

Acid formation would also be the fate of benzaldehyde and cinnamaldehyde if these were processed under vanillin-from-lignin recovery conditions.

The availability of vanillin from lignin is not restricted to spent acid sulfite pulping liquor. It may also be recovered by extraction with an alcohol from the preconcentrated spent black liquor of kraft (sodium hydroxide–, sodium sulfide–based) or soda-based pulping operations, according to a patent filed after the developments described here (*23*). However, chemical and energy recovery from kraft black liquor is so straightforward in comparison to the procedures required for spent acid sulfite liquor recovery that there is less incentive to practice this technology.

As less expensive substrates than eugenol were developed for synthetic vanillin production, the price of vanillin came down (Table 2). This, in turn, served to increase the market for synthetic vanilla flavor and also opened up a number of additional uses of vanillin as chemical intermediate that would not have been attractive at the introductory prices of synthetic vanillin from eugenol. Some idea of the dramatic shift in uses will be appreciated when it is realized that prior to 1960 85% of synthetic vanillin was used for flavors production, whereas by 1970 more than 50% was employed as a chemical intermediate (Table 3). Fortunately for natural vanilla producers, the decreased prices and increased production of synthetic vanillin scarcely affected the production or the market of vanilla beans for flavoring use. Minor constituents in the natural product produce flavor elements in the food that continue to be much appreciated by epicures, particularly when cost is no object.

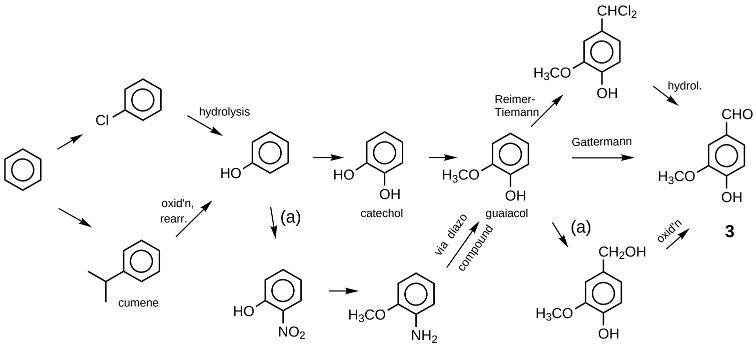


Figure 4. Outlines of petrochemical options to vanillin, **3**, starting with benzene. Quantitative details of pathway (a) have been published (*29*).

Environmental Concerns

The initial development of ethanol and vanillin product recovery sequences for waste sulfite liquor was partially motivated by an interest in decreasing the solubilized sugars and lignin content (the biochemical oxygen demand or BOD properties) of the spent liquor. Increased environmental concerns of the late 1970s and the 1980s led to expedient agreements between vanillin-from-lignin operations and kraft pulping operations (*28*). “Vanillin black liquor” (the spent liquor after vanillin recovery) was shipped from the vanillin plant to the kraft pulp mill, where it was evaporated and burned in the recovery boiler. This mineralized the vanillin black liquor while providing energy recovery and sodium sulfide, useful products for the kraft operation. Increased shipping costs and hazards, plus an increasing mismatch in the sodium to sulfur ratio in the inorganic residue left from combustion of vanillin black liquor, led to the lapse of even these apparently mutually agreeable arrangements. This aspect, the need to safely get rid of 160 kg of “caustic liquids” for each kilogram of vanillin produced, is the principal factor that has now led to the closure of all remaining vanillin-from-lignin plants in Canada and the United States (*25*). The Thorold plant closed in 1987, and facilities in the Seattle area closed in 1991. However, lignin is still used for a substantial portion of the vanillin production of Borregaard Industries, of Sarpsborg, Norway, and perhaps by some other smaller commercial operations. It seems to be counterintuitive, in this age of interest in renewable sources of raw material, that a semisynthetic route to vanillin from a lignin (waste stream) source should fall out of favor in this way.

These negative developments in lignin-based routes to synthetic vanillin, which originally replaced eugenol-based routes, are now being replaced by guaiacol-based routes using petroleum as the original source of the carbon (Fig. 4). Quantitative details of an early version of this process have been published (*29*). Even though this development means that synthetic vanillin is now derived from a nonrenewable source, the far lower volume and easier treatability of the waste streams that are produced by this route apparently more than compensate for this. Nevertheless, the story of vanillin-from-lignin is not over; it is still in commercial use, although not in North America. If innovations can be found that decrease the waste stream problems of these processes they may yet be used again on the large scale that they once were. It is hinted that the Borregaard vanillin-from-lignin plant employs an ultrafiltration technology to fine tune a process developed by Monsanto, which as a result achieves a reduction in waste stream volume (*9, 30*). If one medium-sized pulp mill of the mid-eighties was able to supply 60% of the world market, the potential for vanillin production by these processes is truly vast.

Acknowledgments

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Note

1. Invited presentation “Vanillin from Waste Sulfite Liquor: A Case of the Tail Wagging the Dog” to the 78th Canadian Society for Chemistry Conference and Exhibition, University of Guelph, Guelph, ON, May 28–June 1, 1995.

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