HHS Public Access

Author manuscript

Chem Res Toxicol. Author manuscript; available in PMC 2022 August 05.

Published in final edited form as:

Chem Res Toxicol. 2020 October 19; 33(10): 2489–2490. doi:10.1021/acs.chemrestox.0c00412.

Electronic Cigarettes Are Chemical Reactors: Implication to Toxicity

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Dear Editor, Electronic cigarettes (ECIGs) are a class of products that generate inhalable aerosols by heating a liquid with an electrically powered metallic/ceramic coil. Since their introduction, ECIGs frequently have been compared to combustible cigarettes in terms of the two products' purported differences or similarities in nicotine delivery, abuse liability, and/or toxicant emission. Results of such comparisons encouraged ECIG proponents and some public health authorities to promote ECIGs as less lethal relative to their combustible counterparts. Furthermore, the fact that ECIGs operate at lower temperatures and emit fewer smoke toxicants compared to combustible cigarettes suggested to proponents that ECIGs should be described using toxicity-neutral terms like "nicotine vaporizers", "vaporized nicotine products", "electronic vapor products", "vapes", and "vape pens". In this communication, we argue, based on the mechanisms of formation of toxicants, that ECIGs are described more accurately as chemical reactors: devices where mass transfer, diffusion, and heat transfer along with chemical reactions may occur. That ECIGs involve mass transfer, diffusion, and heat transfer is indisputable,[1] so here we focus on chemical reactions such as pyrolysis and pyrosynthesis.

Regardless of being a heterogeneous product class, ECIGs are generally similar in the composition of their liquid that is composed mainly of propylene glycol (PG) and/or vegetable glycerol (VG), nicotine, and flavorants. Despite this relatively simple set of

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Disclosure statement. Drs. Eissenberg and Shihadeh are paid consultants in litigation against the tobacco industry and the electronic cigarette industry. They are named on a patent for a device that measures the puffing behavior of electronic cigarette users. Also, Dr. Eissenberg is named on another patent for a smartphone app that determines electronic cigarette device and liquid characteristics. The other authors have no competing interests to declare.

constituents, other toxicants have been found in ECIG aerosol, including carbonyls, reactive oxygen species (ROS), radicals, and volatile organic compounds (VOCs), with some studies also reporting the detection of trace amounts of tobacco-specific nitrosamines (TSNAs) and polycyclic aromatic hydrocarbons (PAHs). The source of these toxicants in ECIG aerosols is both the direct distillation of contaminants from ECIG liquids and chemical transformations of PG/VG and other constituents leading to the formation of new chemical compounds. Although recently challenged, PG and VG remain a major source of toxicants in ECIG aerosols, suggesting that toxicant emission is intrinsic to the product class.

The most discussed chemical transformation mechanism of PG and VG is the pyrolysis type of reactions that include oxidation, dehydration, and thermal degradation. These reactions can explain the formation of smaller molecules from PG and VG (carbonyls, ROS, radicals, and some VOCs),[2] but are unable to describe the formation of molecules that have more atoms than PG and VG (some VOCs and PAHs). The formation of these larger molecules may be due to a pyrosynthesis mechanism. As reviewed below, published evidence suggests that both pyrolysis and pyrosynthesis occur within an ECIG, supporting the contention that these products are best characterized as chemical reactors.

We and others have presented evidence demonstrating conclusively that pyrolysis can occur when an ECIG is activated. This evidence included a pyrolytic simulation study of carbonyl formation from PG thermal degradation in a quartz pyrolysis chamber,[3] and the detection of pyrolysis products like CO and small hydrocarbon gases including acetylene and ethylene in the gas phase of ECIG aerosols generated by heating PG and VG.[4] Also, physical determinants of the degradation reactions were identified to be dependent on the coil geometry and its impact on heat dissipation[5] and the heat flux that determines toxicant emissions from ECIG. Indeed, we are currently working to propose a certain upper bound of heat flux as a potential regulatory approach to reduce ECIG toxicant emissions. Similar studies were reported by other groups with one report giving a very detailed account of solvent chemistry in the ECIG reaction vessel.[2] The observation that pyrolysis can occur within an ECIG upon activation is consistent with the notion that these products are chemical reactors. Moreover, we showed that, like a chemical reactor, the more the feed, the greater the products, as illustrated by the high correlation between aldehyde emissions from ECIGs and the amount of liquid consumed (Figure 2 in [5]). These observations are vital to a comprehensive understanding of the toxicity profile of ECIG aerosols.

In addition, we reported evidence of pyrosynthesis taking place upon ECIG activation. The formation of phenolic compounds in ECIG aerosols generated from liquids made of PG/VG recently was shown to be significantly associated with power, puff duration, and mass of generated aerosols.[6] Hence, the formation of phenols is attributed to thermally-driven synthesis from smaller molecules or intermediates (i.e., PG, VG, and their degradation products). In contrast, phenol formation in the smoke of combustible tobacco products is attributed to the pyrolysis of larger molecules like quinic acid, chlorogenic acid, and quercetin. Other ECIG-specific examples of pyrosynthesis include the formation of chloropropanols from the degradation of the sucralose additive in ECIG. The hydrochloric acid generated from the thermal degradation of sucralose reacts with PG and VG to give chloropropanols.[7] Overall, the observation of pyrosynthesis upon ECIG activation, in

addition to pyrolysis, supports characterizing these products as chemical reactors that may yield the formation of ECIG-specific toxicants or common toxicants with combustible cigarettes but via unique mechanistic routes.

This critical analysis of ECIG toxicant formation calls for considering any ECIG as a chemical reactor. In this reactor, pyrolysis and pyrosynthesis mechanisms follow unique pathways that may produce unique toxicants. The understanding of the formation of ECIG toxicants is necessary for a successful determination of ECIG-specific biomarkers of exposure. More work is needed to elucidate the various mechanisms of toxicant formation in ECIG aerosols, mainly using isotopic labeling, additive-toxicant correlations, and chemical kinetic modeling. Highlighting the conditions and mechanisms of toxicant formation is of high importance for predicting the toxicity of ECIGs, and thus implementing evidence-based regulations that minimize toxic emissions from these devices.

Funding.

This research is supported by grant number U54DA036105 from the National Institute on Drug Abuse of the National Institutes of Health and the Center for Tobacco Products of the U.S. Food and Drug Administration. The content is solely the responsibility of the authors and does not necessarily represent the views of the NIH or the FDA.

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