Carbohydrate Polymers 101 (2014) 769–775

Contents lists available at ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol

Review

A review on engineering of cellulosic cigarette paper to reduce carbon monoxide delivery of cigarettes

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ARTICLE INFO

Article history:
Received 1 August 2013
Received in revised form
13 September 2013
Accepted 18 September 2013
Available online 8 October 2013

Keywords:
Cellulosic cigarette paper
Tobacco products
Carbon monoxide delivery
Smoking
Mainstream smoke

ABSTRACT

In cigarette production, the cellulosic paper essentially derived from flax fibers or other fiber materials is used as the wrapping material. During smoking of cigarettes, the highly toxic carbon monoxide is produced. To decrease the amount of carbon monoxide emission in the mainstream smoke, the engineering of all cigarette components including cellulosic cigarette paper and tobacco column is critical. This review summarizes the concepts related to engineering of cigarette paper. These mainly include permeability control, increased use of burn additives, optimization of fiber basis weight, engineering of calcium carbonate fillers, and incorporation of catalysts/oxidants. In particular, catalytic and/or oxidative conversion of carbon monoxide to carbon dioxide has been very widely reported. The control of permeability/diffusivity of cigarette paper is also of critical importance for enhanced diffusion of carbon monoxide out of the cigarette. The development of new concepts and combination of various concepts may lead to breakthroughs in this area.

Contents

1. Introduction

Cigarettes are typical products made from tobacco (Gao et al., 2013; Reddy, Dwivedi, & Sharma, 2012). The practice of cigarette smoking is prevalent all over the world, particularly in developing countries (Abdullah & Husten, 2004). However, during smoking the smokers are indeed initiating a dangerous "chemical plant" around them, in which over 4000 chemicals are released from chemical reactions via various routes (Li, Shen, Qian, & Ren, 2013; Li et al., 2012). Examples of the toxic chemicals in the smoke are carbon dioxide, ammonia, arsenic, hydrogen cyanide, nicotine, and nitrosamines. Essentially, there are two main types of cigarette smoke: mainstream smoke exhaled by the smokers, and sidestream smoke coming from the tip of the burning cigarette (Crocker, 2005). In the context that smoking is likely to continue its prevalence around the globe at least in the near future, the reduction in the toxic emissions (Marcilla, Martínez, Berenguer, Gómez-Siurana, & Beltrán, 2012; Piadé, Wajrock, Jaccard, & Janeke, 2013) in these two streams is critical for mitigating the negative impacts of smoking.

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0144-8617/$ – see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.carbpol.2013.09.101

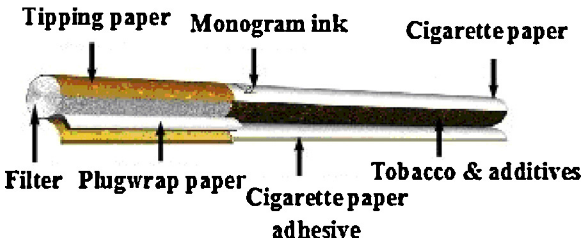

Fig. 1. Schematic of typical components of a cigarette.

As one of the key constituents in cigarette smoke most likely to contribute to the health hazards of smoking, carbon monoxide is mainly formed by several reactions in the combustion/pyrolysis process: oxidation of nonvolatile carbonaceous matter, reductive conversion from carbon dioxide, and pyrolysis of nonvolatile organic matter (primarily cellulosic materials) (Baker, 1977, 1983, 2006; Hoffmann, Adams, & Wynder, 1979). The carbon monoxide in the cigarette smoke is poisonous, and it can decrease the oxygen carried by red blood cells (erythrocytes) throughout the body (Walter Reed Army Medical Center, 2010), potentially causing various diseases including cancer. Thus, there is a strong need to reduce the carbon monoxide emission of smoking.

For the commercial production of cigarettes, it is well-known that the cellulosic cigarette paper is used as the wrapping material for the tobacco column. This specialty paper may also be called cigarette wrapper or cigarette wrapping paper (see Fig. 1, which is downloadable from http://www.soc.duke.edu/~s142tm12/composition_of_a_cigarette.htm), and it acts to hold the tobacco column together. The main components of this cellulosic material are: pulp fibers (typically flax or wood fibers), filler material (typically calcium carbonate), and burn rate modifier (typically sodium or potassium citrate) (Podraza, 2001). As a bio-based material derived from natural resources, flax fibers (Duigou, Bourmaud, Balnois, Davies, & Baley, 2012; Garcia-Ubasart, Torres, Vila, Pastor, & Vidal, 2013) are used in the production of cigarette paper. Commercially, a papermaking process involving forming paper sheets on the papermaking wires by dewatering the furnishes, drying the paper sheets, and finishing was applied to produce the cigarette paper products. The scanning electron micrograph (SEM) images of a typical cigarette paper product are shown in Fig. 2, in which the cellulosic fibers and filler particles can be seen.

The cigarette paper plays an important role in the manufacture of cigarettes, and its physical properties are critical for acceptable runnability of the cigarette making machine (Case & Astl, 2003). Also, the appearance of cigarettes is dependant upon the characteristics (e.g., opacity and brightness) of cigarette paper (Case & Astl, 2003). On the other hand, it is interesting to note that the emissions of carbon monoxide and other compounds during smoking can be dependant on the characteristics of cigarette paper (Bernhard, 2011). By engineering of the cigarette paper and/or other parts of a cigarette, there is a possibility to tune the levels of toxic emissions (Li et al., 2013; Liu et al., 2011; McAdam et al., 2011). The aim of this paper is to give a review of the reported concepts related to engineering of cigarette paper for reducing the carbon monoxide delivery in the mainstream smoke of cigarettes.

2. Increasing the air permeability of cellulosic cigarette paper

Cellulosic paper is essentially a three-dimensional network consisting of cellulosic fibers, calcium carbonate, and other components. This network has a porous nature. In general, the porosity of cigarette paper determines its air permeability, and the latter is related to the passing of air through the paper sheet under a pressure difference. It is widely-known that by increasing the air permeability of the porous paper, the carbon monoxide formation can be discouraged (Hoffmann et al., 1979; Kozlowski & O'Connor, 2002; Robinson & Forbes, 1975; Rostami & Hajaligol, 2003; Stephens, 2007). This has been thought to be attributed to the so-called "air dilution" effect of the porous cigarette paper (Hoffmann et al., 1979); essentially, during the draw phase air flows through the cigarette paper into the inside of the cigarette, thereby causing a dilution of the cigarette smoke and thus a reduction of the smoke concentration (Schneider, Pangritz, & Riedesser, 1985). This "air dilution" effect results in the diffusion of carbon monoxide out of the cigarette (Baker & Crellin, 1977). It may also be reasonable that at a high air permeability, the oxygen levels in cigarettes is high, thus facilitating the conversion of carbon monoxide to carbon dioxide. In one study, the increase in porosity from 25 to 100 CU resulted in a decrease in carbon monoxide delivery from about 15.5 to about 12 mg/cig. (LTR Industries, 1981). Here, CU refers to Coresta unit. Coresta is an association founded in 1956, ruled by French law, the purpose being to promote international cooperation in scientific research relative to tobacco (http://www.coresta.org/). A Coresta unit is a measure of cigarette paper permeability, defined as the flow ($cm^3\,min^{-1}$) passing through a 1 cm^2 sample of test material at an applied pressure of 1.00 kPa. In this case, in terms of practical applications, the porosity/air permeability of cigarette paper and carbon monoxide delivery can be tuned by optimizing the use of fibers and chemicals (e.g., calcium carbonate). As a matter of fact, this concept has been commercially practiced. However, as air permeability increases, the hydrogen bonding of the paper sheet is negatively impacted. Another challenge is that the increase in air permeability may negatively influence the taste of the cigarette (Schneider et al., 1985). Thus, there is a limit that carbon monoxide delivery can be reduced by increasing the air permeability of cigarette paper.

3. Increasing the dosage of burn additives in cellulosic paper

Burn additives are typically used in the production of cigarette paper. Their use can regulate the burning characteristics of the paper, and the burning can be faster during smoking. Typical burn additives (LTR Industries, 1981) are sodium/potassium citrate, sodium acetate, sodium phosphate, etc. The application of some burn additives (e.g., citrate) reduces the number of puffs, and hence carbon monoxide delivery can be expected to be decreased, and in a certain range (e.g., 0.5–3 wt.%, based on the dry weight of cigarette paper) the increase in dosage of burn additives have been reported to result in reduced carbon monoxide delivery (LTR Industries, 1981). This concept may easily be practiced in the paper industry. However, the increased carbon monoxide delivery per puff as a result of the increase in the dosage of burn additives mitigates this, and thus an overall trend is that the positive role of burn additives in reducing carbon monoxide delivery is not quite pronounced. Also, the taste of the cigarette may also be influenced by the increased use of burn additives (Schneider et al., 1985).

4. Decreasing the fiber basis weight of cellulosic cigarette paper

In the paper industry, saving of cellulosic fibers is important for decreasing the manufacturing cost and the carbon footprint of paper products (Baum, 2002; Shen, Song, Qian, & Liu, 2010). In the case of cigarette paper, decreased amount of fibers per cigarette, i.e., decreased fiber basis weight, has been reported to be favorable for reducing carbon monoxide delivery (Hampl, 2004). Table 1 shows the exemplifying results related to this concept. The mechanism

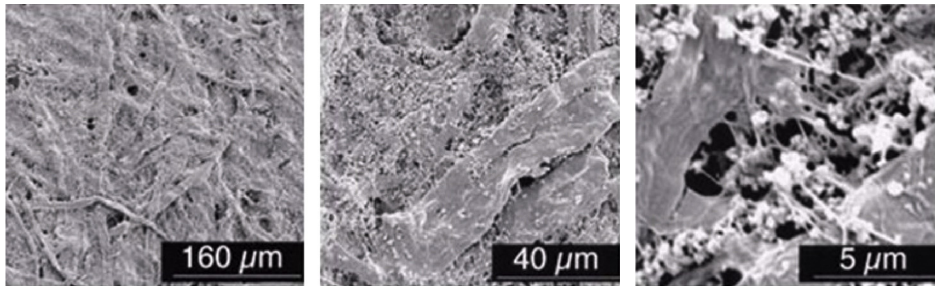

Fig. 2. Scanning electron micrograph images of a typical cigarette paper product (Branton & Baker, 2002).

associated with such a decrease in carbon monoxide delivery as a result of decreased fiber basis weight has not been reported. Two reasons might be responsible for this. Firstly, once the amount of fibers per cigarette decreases, the formation of carbon monoxide from fibers can be discouraged. Secondly, decreased basis weight may sometimes initiate the increase in permeability (see Table 1), thus decreasing the carbon dioxide delivery as a result of enhanced air dilution and increased oxygen levels.

5. Optimizing the use of calcium carbonate in cellulosic cigarette paper

The use of mineral fillers and pigments in the paper industry is a well-known practice (Deng, Jones, McLain, & Ragauskas, 2010; Hubbe & Gill, 2004; Li, Li, & Lu, 2010; Shen, Song, Qian, & Liu, 2009). The incorporation of fillers in the paper sheet can reduce the product cost (including energy saving) (Dong, Song, Patterson, Ragauskas, & Deng, 2008), and improve the traditional properties (i.e., optical properties, printability, and writability) of paper. Fillers can also be used to deliver functional applications (e.g., magnetic, photo-catalytic, deodorizing, and flame retardant properties) to cellulosic paper (Shen, Song, Qian, & Ni, 2011). The so-called filler engineering concept involving every possible aspect of modifying/improving/upgrading the characteristics of fillers/filler-containing composites, or the development of new types of fillers, for papermaking applications, is an active research area (Cao, Song, Deng, & Ragauskas, 2011; Deng et al., 2010; Fatehi, Hamdan, & Ni, 2013; Fatehi, Shen, Hamdan, & Ni, 2013; Huang, Shen, & Qian, 2013; Lin, Yin, Nazhad, & Lehtinen, 2010; Shen & Qian, 2012; Shen, Song, & Qian, 2009; Shen, Song, Qian, & Liu, 2009; Shen, Song, Qian, Liu, & Yang, 2010; Shen et al., 2011; Shen, Song, Qian, & Yang, 2010; Song, Zhang, He, Li, & Ni, 2012; Zhao, Hu, Ragauskas, & Deng, 2005). The development and commercialization of new filler engineering technologies may be useful to lead to breakthroughs in the area of pulp and paper. The use of calcium carbonate as a filler material in cigarette paper is well known. Calcium carbonate is a non-toxic inorganic material, and hence it can be safely added in cigarette paper. The addition of calcium carbonate is also critical for improving the opacity and brightness/whiteness of cigarette paper, allowing for decreased basis weight and improved appearance. Another benefit of adding calcium carbonate to cigarette paper is related to the artistic aspects of cigarette smoking, i.e., ensuring the formation of an attractive ash during smoking (Browne, 1990). Additionally, the use of calcium carbonate can control the porosity and burning rate of cigarette (Holik, 2006). Commercially, there are two categories of calcium carbonate: ground calcium carbonate and precipitated calcium carbonate. Of these two, precipitated calcium carbonate is usually a preferred choice for the production of cigarette paper (e.g., in the case of cigarette paper manufactures in China).

The carbon monoxide delivery of cigarettes can be dependant upon the added amount of calcium carbonate. In one study, it was reported that higher calcium carbonate content of the cigarette paper induced lower carbon monoxide delivery (Baldwin et al., 1992). Thus, in the case of commercial application, the added amount of calcium carbonate can be as high as possible. As calcium carbonate has a lower cost than pulp fibers, adding more calcium carbonate to paper also provides a possibility to reduce the product cost. However, due to the negative effect of filler addition on fiber–fiber bonding and hence paper strength, there is a limit for the added amount. In general, based on the current situation, it is possible to add as much as 30–40 wt.% calcium carbonate to cigarette paper. In the case of high filler addition levels, paper strength can be maintained by optimizing the fiber components, adding strength additives (e.g., carboxymethyl cellulose and cationic starch), etc. (Fatehi, Kititerakun, Ni, & Xiao, 2010; Fatehi, Tutus, & Xiao, 2009; Liu, Fatehi, Ni, & Xiao, 2010).

In the filler engineering concept, combination of different types of fillers for performance balancing is very interesting, particularly from the practical point of view (Shen, Song, Qian, Liu, & Yang, 2010). Encouragingly, in a recent study, it was reported that the combination of two calcium carbonates with different mean particle sizes (one has the mean particle size of 0.1–2 μm, and the other has the mean particle size of 3.5–10 μm) significantly reduced the carbon monoxide delivery (Fritzsching, 2009). The exemplifying results are shown in Table 2. It was also noted that such a combination could result in a decrease in carbon monoxide

Table 1
Carbon monoxide deliveries of cigarettes prepared from cigarette paper samples with varied fiber basis weights (Hampl, 2004).

Sample	1	2	3	4
Basis weight (g/m^2)	21	19	18	17
Calcium carbonate (%)	21	23	23	21
Fiber basis weight (g/m^2)	16.4	14.6	13.9	13.4
Permeability (CU)	30	42	70	86
Citrate (%)	0	0	0	0
Carbon monoxide delivery (mg/cig.)	13.1	11.8	11.2	10.6

Table 2
Carbon monoxide deliveries of cigarettes prepared from cigarette paper samples (based on different filler addition methods) (Fritzsching, 2009).

Sample	1	2
Burn additive	Sodium acetate	Sodium acetate
Air permeability (CU)	60	60
Filler content (wt.%)	33	33
Basis weight (g/m^2)	25	25
Filler addition	Filler A[a]	Filler B + Filler C[b]
Carbon monoxide delivery (mg/cig.)	8.2	6.7

[a] The added filler material was made up of 100% of Precarb 122VP (mean particle size of 1.6 μm as per sedigraph measurement, Schaefer Kalk, Dietz).

[b] The added filler material was made up of 80% of Precarb 720 (mean particle size 0.5 μm as per sedigraph measurement, Schaefer Kalk, Dietz) and 20% of Precarb 160 G (mean particle size of 4.2 μm as per sedigraph measurement, Schaefer Kalk, Dietz) (Precarb 122VP, Precarb 720, and Precarb 160 G are commercial products of calcium carbonate).

delivery without altering the air permeability of the cigarette paper (the calcium carbonates were incorporated in a suitable mixing ratio). Thus, such a decrease in carbon monoxide delivery was not due to the increase in air permeability. This encouraging finding may provide an interesting alternative to the reduction of carbon monoxide delivery. The interesting role of filler combination may be understood from the diffusivity point of view. There are distinct differences between diffusivity and permeability. Diffusivity is a measure of diffusion of gases through the cigarette paper under no pressure difference. However, air permeability is measured under a pressure difference (Hamamoto, Tokida, Miyazaki, & Mizoguchi, 2008; Jia, 2012).

Filler particle shape/morphology can have an impact on the properties of filled papers (Hubbe & Gill, 2004). The morphology/shape of calcium carbonate particles can also influence the carbon monoxide delivery of cigarettes. The use of columnar or acicular particles has been reported to have lowered carbon monoxide delivery, as compared with the spindle-shaped particles (Ishikawa, Yoshimura, & Sasakawa, 2012). This interesting finding may be useful in selecting the right calcium carbonate for use in cigarette paper. In this sense, shape-controlled synthesis of calcium carbonate is critical.

Mechanistically, the influence of the morphology/shape/combinations of calcium carbonate particles may be understood in terms of the combined/integrated role of diffusivity and permeability of cigarette paper in carbon monoxide delivery.

6. Incorporation of catalysts to cellulosic cigarette paper

Essentially, to reduce the carbon monoxide delivery of cigarettes, its oxidation during smoking is an important concept. In the general field of chemistry and chemical engineering, the use of metal catalysts for catalytic oxidation of the highly toxic carbon monoxide to less toxic carbon dioxide has been widely concerned (Alayoglu, Nilekar, Mavrikakis, & Eichhorn, 2008; Bharali, Saikia, Katta, & Reddy, 2013; Imanaka, Masui, Imadzu, & Yasuda, 2011; Kim, Han, & Choi, 1979; Lin & Chen, 2005; Royer & Duprez, 2011; Xie, Li, Liu, Haruta, & Shen, 2009). In the case of decreasing carbon monoxide delivery of cigarettes by catalytic oxidation, a large number of publications are available in the literature (Deevi & Ettireddy, 2007; Deevi & Koller, 2004a, 2004b; Deevi & Pillai, 2009, 2010; Dimitur, Lvanka, & Mariyana, 2004; Gedevanishvili & Rabiei, 2007; Gedevanishvili, Reddy, Pithawalla, & Paine, 2007; Imai et al., 2012; Li & Hajaligol, 2003; Li, Rasouli, & Hajaligol, 2004a, 2004b; Li, Gedevanishvili, et al., 2007; Li, Rasouli, Gedevanishvili, & Zhang, 2007; Li, Rasouli, & Hajaligol, 2007; Luan et al., 2004; Miser & Gee, 2012; Rasouli, Li, Tafur, et al., 2005; Rasouli, Li, Zhang, & Gedevanishvili, 2005; Reddy, Rasouli, Hajaligol, & Khanna, 2010; Rongved, 1997; Saoud, Rasouli, Rabiei, Gedevanishvili, & Hajaligol, 2009; Sundar & Deevi, 2010; Yadav, Saoud, Rasouli, & Hajaligol, 2012; Zhou, Shen, Chu, Zhan, & Guo, 2011). The decreased carbon monoxide delivery can be achieved by adding catalysts to a portion or all components (including cigarette paper, tobacco rod, and filter) of cigarettes. In theory, addition to all components may result in even lower carbon monoxide delivery. However, the addition of catalysts to different parts of a cigarette has different requirements. For instance, when added to the cigarette filter, a high catalytic activity at room temperature is required.

Various water-insoluble inorganic catalysts including metals, metal oxides, or oxy-hydroxides have been incorporated to cigarette paper to decrease carbon monoxide delivery (Deevi & Koller, 2004a, 2004b; Deevi & Pillai, 2009, 2010; Gedevanishvili & Rabiei, 2007; Gedevanishvili et al., 2007; Imai et al., 2012; Li, Rasouli, Gedevanishvili, et al., 2007; Li, Rasouli, & Hajaligol, 2007; Luan et al., 2004; Rasouli, Li, Tafur, et al., 2005; Rasouli, Li, Zhang, et al., 2005; Reddy et al., 2010; Saoud et al., 2009; Sundar & Deevi, 2010; Yadav et al., 2012). In this regard, iron-based particles such as Fe_2O_3 are one of the most frequently reported catalysts, while the use of noble metal-based particles such as Ag_2O has also been reported (Sundar & Deevi, 2010). Although Fe_2O_3 is frequently reported as typical for iron-based catalysts, Fe_3O_4 may also be a demonstrable option (Li, Rasouli, Gedevanishvili, et al., 2007). Al_2O_3 and CuO can function as oxidation catalysts for conversion of carbon monoxide to carbon dioxide, and their activities are in general not be as high as Fe_2O_3. However, the catalytic activity of CuO is much higher than that of Al_2O_3 (Li, Rasouli, Gedevanishvili, et al., 2007). There are several ways of incorporating these catalysts to cigarette paper: direct wet-end addition of catalyst particles, in situ synthesis of catalyst particles in papermaking process, application of catalyst particles/precursors via size-press, vapor deposition or printing, etc. (Deevi & Koller, 2004a, 2004b; Gedevanishvili & Rabiei, 2007; Li, Rasouli, & Hajaligol, 2007; Luan et al., 2004; Rasouli, Li, Tafur, et al., 2005; Rasouli, Li, Zhang, et al., 2005; Saoud et al., 2009; Sundar & Deevi, 2010; Yadav et al., 2012). Compared with the wet-end or internal application of catalyst particles, surface application may be preferred due to their better retention and potentially higher catalytic efficiency as a result of preferential enrichment near the paper surface other than the inner side of paper. Also, the controlled and patterned deposition of catalyst particles on cigarette paper via surface addition (e.g., via printing) is likely to result in a product with possible artistic attractiveness. During smoking, in the presence of oxygen these catalysts can increase the rate of oxidation of carbon monoxide; on the other hand, in the absence of oxygen they may also function as an oxidant, i.e., by donating oxygen to the reactant (Li, Rasouli, & Hajaligol, 2007).

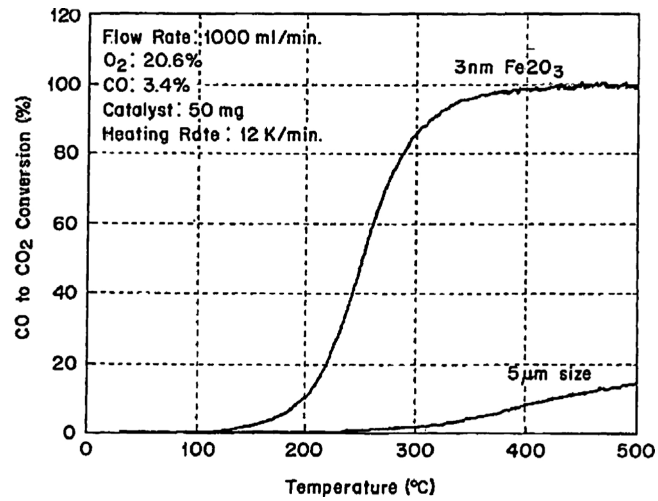

Fig. 3. Catalytic activities (in terms of conversion of carbon monoxide to carbon dioxide) of Fe_2O_3 particles of different particles sizes (Li, Gedevanishvili, et al., 2007).

It is noteworthy that in the case of Fe_2O_3 catalyst used for the conversion of carbon monoxide to carbon dioxide, its catalytic activity has been reported to be highly dependant upon the particle size. In general, smaller-sized particles exhibit better catalytic activity. Fig. 3 shows the comparison between the catalytic activity of Fe_2O_3 nanoparticles having an average particle size of about 3 nm, versus Fe_2O_3 powder having an average particle size of about 5 μm, and it is evident that the use of the nanoparticles can be preferred (Li, Gedevanishvili, et al., 2007).

The pore size of porous Fe_3O_4 catalytic particles has been reported to be critical for efficient carbon monoxide conversion (Imai et al., 2012). Essentially, if the pore size is too large (e.g., larger than 20 nm), the contact efficiency of carbon monoxide and catalyst

Table 3
Carbon monoxide deliveries of cigarettes prepared from cigarette paper samples (based on the use of unmodified and modified calcium carbonate fillers) (Rasouli, Li, Zhang, et al., 2005).

Sample	1	2	3
Catalyst loading in web-filler (wt.%)	0	25	50
Filler addition level (either $CaCO_3$ web-filler material or catalyst modified web-filler) (wt.%)	30	30	30
Targeted basis weight of cigarette paper (g/m^2)	35	35	35
Carbon monoxide delivery (mg/cig.)	16.6	11.6	9.5

particles is deteriorated. On the other hand, if the pore size is too small (e.g., less than 2 nm), water molecules necessary for a shift reaction ($CO + H_2O \rightarrow CO_2 + H_2$) scarcely penetrate into the pores, and the efficiency of the catalyst particles is deteriorated.

The morphology/shape of catalyst particles may influence their use in cigarette paper. The fabrication of catalyst particles having a two-dimensional shape (e.g., fibrous shape) is expected to improve paper sheet formation, when they are added to paper in the papermaking wet-end section (Saoud et al., 2009).

It is likely that the catalyst particles can be partially contaminated and/or deactivated during smoking or over long periods of storage (Gedevanishvili et al., 2007; Rasouli, Li, Tafur, et al., 2005). During smoking of cigarettes containing catalyst particles, semi-volatile or non-volatile combustion products such as tar can form on the catalyst particles, and thus their deposition can reasonably deactivate the catalyst particles (Gedevanishvili et al., 2007). In this case, metal oxy-hydroxides may be a better choice than metal oxides, since the former (e.g., FeOOH) can decompose to form the latter (e.g., Fe_2O_3) and water at temperatures typically reached during smoking (e.g., above 200 °C) (Rasouli, Li, Tafur, et al., 2005). Similarly, the encapsulation of catalyst particles with such polymers as sodium alginate may improve their catalytic activity during smoking, as the early evaporation of these encapsulants can prevent the deposition of such compounds as tar on the catalyst particles (Gedevanishvili et al., 2007).

The combination of nanoparticle Fe_2O_3 catalyst with calcium carbonate to form a composite filler material for cigarette paper has been reported (Rasouli, Li, Zhang, et al., 2005). It has been found that with the increase in loading level of the catalyst, carbon monoxide delivery can be decreased. Some typical results are shown in Table 3. As shown in Table 3, the use of the catalyst with the loading level of 50 wt.%, i.e., half of the amount of calcium carbonate, resulted in a decrease in carbon monoxide delivery by about 40%. Here, calcium carbonate may acts as a mechanical support for the catalyst particles. The supporting of catalyst particles with such supports as high-surface-area silica gel for the fabrication of composite catalysts is a very interesting concept, and the support particles may act as a separator, which can inhibit diffusion, agglomeration, or sintering together of the supported catalyst particles before or during combustion of the cigarette paper during smoking (Deevi & Koller, 2004a, 2004b; Luan et al., 2004; Miser & Gee, 2012). Also, as the support material minimizes sintering of the catalyst particles, its presence can minimize the loss of the active surface accessible for the catalytic function (Miser & Gee, 2012). Optionally, the combination of different catalysts with varied characteristics may provide a possibility for performance balancing (Deevi & Pillai, 2009).

It should be stated that although the addition of catalysts to cigarette paper can reduce the carbon monoxide delivery to a certain degree, its cost-effectiveness may still need to be improved, so that the commercial application of the relevant technologies can be moved forward. Also, the catalysts (e.g., Fe_2O_3 nanoparticles) significantly effective in reducing carbon monoxide delivery are mainly colored materials, and hence their use can affect the appearance of the cigarette paper, which may not be promising in terms of commercial use, particularly when product standards/legislations (e.g., in terms of paper appearance) are taken into account (Fritzsching, 2009). Thus, there is still a need to develop more cost-effective and commercially applicable catalysts that can easily be added to cigarette paper. Nevertheless, the concept of incorporating catalysts and/or oxidants to cigarette paper together with other cigarette components (essentially tobacco and cigarette filter) is rather promising, and further research and development in this area is expected to lead to technological breakthroughs in this area.

7. Other concepts related to engineering of cellulosic cigarette paper

For decreasing the carbon monoxide delivery of cigarettes by engineering of cellulosic cigarette paper, in addition to the above mentioned concepts, other concepts are also available in the literature (Dixit, 1986; Volgger, 2012).

The addition of non-ionic surfactants to cigarette paper by surface application has been found to reduce carbon monoxide delivery; however, the mechanism has not been fully understood. It was theorized that they stabilize the moisture content of the paper at a level incompatible with efficient carbon monoxide production on burning (Dixit, 1986). Examplarily, the surface application of a nonionic surfactant (i.e., the commercial product of PG-2601 from Olin Corp. produced by randomly condensing glycerol with ethylene oxide and propylene oxide and finally capping the hydroxyl ends thereof with ethylene oxide) with a concentration of 5% (w/v) to cigarette paper resulted in a decrease of carbon monoxide delivery from 16.0 to 14.2 mg/cig (Dixit, 1986). Also, in a recent study, the addition of a water-soluble salt, preferably sodium bicarbonate, potassium bicarbonate or ammonium carbonate, to cigarette paper, was found to increase the diffusion capacity of cigarette paper, and thus a decrease in carbon monoxide in cigarette smoke (Volgger, 2012).

It is noted that for the various concepts mentioned in this paper, they may overlap each other in some cases. For example, the optimization of the use of calcium carbonate may result in a change in permeability of the cigarette paper, which is favorable for decreasing carbon monoxide delivery.

8. Concluding remarks

During smoking of cigarettes, a number of chemical compounds are released to the smoke. As one of the toxic components, the reduction in carbon monoxide delivery in the mainstream smoke has been widely concerned. Theoretically, all components of cigarettes including cigarette paper and tobacco column can be engineered to decrease the carbon monoxide delivery. In the case of cigarette paper, various concepts have been proposed; these mainly include: (1) increasing the porosity/air permeability of cigarette paper; (2) increasing the dosage of burn additives; (3) decreasing the fiber basis weight of cigarette paper; (4) optimization of the use of calcium carbonate; (5) incorporation of catalysts and/or oxidants. Such concepts as porosity control and use of burn additives have been commercially implemented. It is noted that in addition to reduction in carbon monoxide delivery, most of the concepts reviewed in this paper may also be simultaneously important for decreasing tar delivery for instance.

In terms of addressing the role of cigarette paper in decreasing carbon monoxide delivery, it is likely that a combined use of several concepts would be useful in practical applications. Fundamental/practical studies related to catalytic oxidation/conversion of carbon monoxide during smoking for instance would be important for the development of more efficient technologies. In this sense, new concepts are expected to be demonstrated and adopted in the future. The incorporation of nontoxic chemical additives would be the key to future breakthroughs in this area. However, cigarette smoking is anyway detrimental to people's health, and hence simply reducing carbon monoxide delivery is not the ultimate goal. The reduction of toxic emissions other than carbon monoxide is also of critical importance. In the long run, more research and development work is needed to mitigate the negative effect of smoking. Meanwhile, more work should be done on smoking banning/cessation, so that this negative impact can be substantially mitigated.

Acknowledgements

The authors would like to acknowledge support from the Fundamental Research Funds (DL12CB08) for the Central Universities of China, the National Natural Science Foundation of China (Grant No. 31100439), the Program for New Century Excellent Talents in University (NCET-12-0811), and the Program for Returned Overseas Chinese Scholars from the Ministry of Human Resources and Social Security of China.

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