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Sohail Yasin

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Mécanique, énergétique et matériaux

Par

Sohail YASIN

ECO-DESIGN FOR END-OF-LIFE PHASE OF FLAME RETARDANT TEXTILES

Dans le cadre du programme Erasmus Mundus Joint Doctorate: *Sustainable Management and Design for Textile*

Thèse co-dirigée par N. Massika BEHARY, Giorgio ROVERO et Guoqiang CHEN

Soutenue le 20 juin 2017 devant la commission d'examen

JURY

Isabelle VROMAN	Professor, ESIREims, France	Referee
Elisabetta ARATO	Professor, Genova University, Italy	Referee
Sophie DUQUESNE	Professor, ENSC-Lille, France	Examiner/Président
Myriam VANNESTE	Director R&D, CENTEXBEL, Belgium	Examiner
Laurent MARMORET	Associate Professor, IUT d'Amiens, France	Examiner
Massika BEHARY	Associate Professor, HDR, ENSAIT, France	Directeur
Giorgio ROVERO	Professor, Polito, Italy	Directeur
Anne PERWUELZ	Professor, ENSAIT, France	Invite
Jinping GUAN	Associate Professor, Soochow University, China	Invite

Eco-design for End-of-Life phase of Flame Retardant Textiles

Ph.D. dissertation by

Sohail YASIN

in partial fulfillment of Erasmus Mundus joint Doctorate Program: SMDTex –
Sustainable Management and Design for Textiles

In collaboration with: ENSAIT – GEMTEX laboratory
University Lille 1 – Department of Materials and Mechanics
Politecnico di Torino – Department of Chemical Engineering
Soochow University – Department of Textile Engineering

Il n'y a qu'un bonheur dans la vie, c'est d'aimer et d'être aimé. (George Sand)

There is only one happiness in the life, to love and be loved.

Preface

This thesis comprehends research done during Ph.D. project conceded out at three universities, ENSAIT – France, Politecnico di Torino – Italy and Soochow University – China, from Sep 1, 2013 to August 31, 2017. Professor Anne Perwuelz, Associate Professor Nemeshwaree Behary, Professor Giorgio Rovero, Associate Professor Jinping Guan and Professor Guoqiang Chen were supervisors. The research project was funded by the SMDTex – Erasmus Mundus program, the European Commission’s initiative. The thesis is systematized in three parts: the first part proposes an eco-design for the end-of-life phase of flame retardant textiles; the second part consists of energy valorization by gasification and third part deals with the comprehensive life cycle assessment (LCA) of the eco-design and gasification of flame retardant textiles. The context of this Ph.D. is derived from the findings of papers listed below. The papers will be referred to in the Ph.D. by paper numbers, written in Roman numerals **I-VI**.

Journal Papers

I: Sohail Yasin, Nameshwaree Behary, Stephane Giraud, Anne Perwuelz. In-situ degradation of organophosphorus flame retardant on cellulosic fabric using advanced oxidation process: A study on degradation and characterization. *Polymer Degradation and Stability* 126 (2016), 1-8. <http://dx.doi.org/10.1016/j.polymdegradstab.2015.12.005>

II: Sohail Yasin, Nemeshwaree Behary, Giorgio Rovero, Vijay Kumar. Statistical analysis of use-phase energy consumption of textile products. *The International Journal of Life Cycle Assessment* (2016), 1-13. <http://dx.doi.org/10.1007/s11367-016-1129-2>

III: Sohail Yasin, Nameshwaree Behary, Massimo Curti, Giorgio Rovero. Global Consumption of Flame Retardants and Related Environmental Concerns: A Study on Possible Mechanical Recycling of Flame Retardant Textiles. *Fibers* 4 (2016), 1-16. <http://dx.doi.org/10.3390/fib4020016>

IV: Sohail Yasin, Massimo Curti, Giorgio Rovero, Nemeshwaree Behary, Anne Perwuelz, Stephane Giraud, Gianluca Migliavacca, Guoqiang Chen, and Jinping Guan.

An Alternative for the End-of-life Phase of Flame Retardant Textile Products: Degradation of Flame Retardant and Preliminary Settings of Energy Valorization by Gasification. *BioResources* 12(3), 5071-5085. doi: 10.15376/biores.12.3.5196-5211

V: Sohail Yasin, Bhavsar Parag, Nemeshwaree Behary, Rovero Giorgio. Optimizing Organophosphorus Fire Resistant Finish for Cotton Fabric Using Box-Behnken Design. *International Journal of Environmental Research* 10 (2016), 313-320.

VI: Sohail Yasin, Curti Massimo, Behary Nemeshwaree, Rovero Giorgio, Guoqiang Chen, Jinping Guan, Anne Perwuelz. Process optimization of eco-friendly flame retardant finish for cotton fabric: A response surface methodology approach. *Surface Review and Letters*. 14 February (2017). <http://dx.doi.org/10.1142/S0218625X1750114117>

Conference Papers

I: Sohail Yasin, Nemeshwaree Behary, Anne Perwuelz, Jinping Guan, Guoqiang Chen. Degradation Kinetics of Organophosphorus Flame Retardant from Cotton Fabric. 2nd ICAMEST 2016 International Conference on Advanced Material and Engineering Structural Technology, Jeju, South Korea (2016).

II: Sohail Yasin, Anne Perwuelz, Nameshwaree Behary. Case study of life cycle inventory of cotton curtain. 14th Autex World Textile Conference, Turkey (2014).

III: Sohail Yasin, Nemeshwaree Behary, Stephane Giraud, Anne Perwuelz. Degradation of phosphorus based flame retardant by IR radiation. 15th Autex World Textile Conference, Bucharest, Romania (2015).

The papers are not included in this version of the thesis but can be found on the particular publishers print or electronic databases.

Abstract

Production, consumption, and disposal of textile products have substantial adverse impacts on the environment, especially textiles with flame retardant (FR) finishes. Unfortunately, information on the exposure of FR from textile products to environmental pathways is scarce. Research works on FR textiles have been mostly focused on ways to provide environmentally friendly synthesis and production phases of FR textile products. However, the end-of-life phase of the FR textiles seems neglected and needs great attention when the product's life cycle is concerned. The end-of-life phase of FR textile products is considered as a hurdle in current sustainable disposals (landfill and incineration), though today, technologies for solid waste management are ever-improving. Indeed, landfill and energy valorization through incineration are considered as suitable pathways for textile wastes, including technical textile wastes. However, the end-of-life of FR textile products creates issues, such as in landfilling, there is a huge chance of FR species or substance leaching to the environment. Similarly, FR species decrease energy yield in the incineration process due to incomplete combustion and emits toxic fumes.

It is essential to find different ways to assess the most optimum methods or eco-designs for the disposal of textile products by energy valorization through gasification. Therefore an eco-design was proposed with optimized disposals for the FR textiles. Eco-design comprises the degradation and elimination of a permanent/durable FR substance from the textiles, especially cellulosic textiles prior to their disposals. Thermal valorization was achieved by gasification instead of incineration, to explore the ability of FRs to gasify after the degradation and elimination of the FR species.

Durable FR species, for instance, *n*-methylol dimethyl phosphonopropionamide (MDPA) is one of the most effective organophosphorus FRs for cellulosic fabrics, used in combination with

trimethylol melamine (TMM) to obtain durable and improved FR properties. The degradation and elimination of an organophosphorus FR (MDPA) on cellulosic fabric, was studied using an advanced oxidation process (AOP) based on Fenton's reaction. The effect of varying concentrations of Fenton's reagents (H_2O_2 and Fe^{2+} in aqueous medium) on the degradation of the MDPA was studied. The degradation of MDPA in aqueous media was monitored by measuring chemical oxygen demand (COD) of the reaction mixture over time. The mechanical properties of the cellulosic fabric after Fenton's reaction were unaltered in both warp and weft directions. The flammability test and thermogravimetric results (TGA, DTG and PCFC) confirmed the degradation of MDPA FR from the fabric.

FR species being degraded and eliminated from the cotton textiles, energy valorization by gasification was carried out for increased energetic yield due to better combustion and potential syngas composition outcomes during the gasification. The gasification results supported the eco-design by showing increased combustion properties of the FR textiles after the degradation and elimination of the FR species. For the sustainability validation of the proposed eco-design, a life cycle assessment (LCA) was performed to analyze the environmental impacts of eco-design for the end-of-life phase of FR textile products. LCA is one of the prominent assessment methods to perform the general assessment of products or services.

The thermogravimetric and pyrolysis combustion results confirm that there is a higher heat release after Fenton's reaction degradation. The heat release rate of the FR cotton textiles increased by 51% after the degradation of the FR species, and this makes the degraded FR cotton interesting for energy valorization. The energy valorization by gasification results supported the eco-design by showing increased combustion properties of the FR textiles after the degradation and elimination of the FR species. Lastly, the LCA results showed reduced impact values in most of the impact categories studied, especially in global warming potential (GWP), air acidification (AA) and in other prominent categories in favor of degradation and elimination of FR species from the textiles and being gasified.

Keywords: Flame retardant; textiles; degradation; oxidation-reduction; gasification; LCA

Résumé

Les différentes phases du cycle de vie d'un produit textile, la production, l'utilisation et la fin de vie, ont des impacts importants sur l'environnement, en particulier lorsque les textiles ont été ignifugés. Malheureusement, les données concernant les produits ignifuges et leur présence dans l'environnement ne sont pas facilement accessibles.

Dans le domaine des produits ignifuges utilisés pour le textile, les nombreuses recherches menées ont été principalement axées sur des méthodes de synthèse et de production de ces molécules afin de les rendre plus respectueuses de l'environnement. Cependant la phase de fin de vie des textiles ignifugés a été longtemps négligée, et nécessite aujourd'hui une attention particulière lorsqu'on effectue une analyse de cycle de vie d'un produit textile. Bien qu'aujourd'hui, les technologies utilisées pour la gestion des déchets solides ne cessent de s'améliorer, la valorisation des déchets par incinération est une voie appropriée pour les textiles, y compris les textiles techniques.

La fin de vie des produits textiles ignifuges pose des problèmes. Lors de la mise en décharge, il existe de nombreuses possibilités de lixiviation des substances ignifuges dans l'environnement. De même, les espèces ignifuges diminuent le rendement énergétique dans le processus d'incinération en raison d'une combustion incomplète et émettent des fumées toxiques.

Il est essentiel de trouver des méthodes optimales écologiques pour la valorisation énergétique des déchets textiles par la gazéification. Nous proposons une méthode plus écologique de valorisation énergétique des déchets textiles ignifugés, par la dégradation et l'élimination préalable des substances ignifuges permanentes des textiles, en particulier des cellulosiques. Ensuite, la valorisation thermique est réalisée par gazéification au lieu de l'incinération. Au bilan, nous discutons la capacité des tissus ignifugés à gazéifier et produire de l'énergie selon les prétraitements effectués. Le n-méthylol diméthylphosphonopropionamide (MDPA) est un

des retardateurs de flamme organophosphorés le plus efficace pour les tissus celluloses, utilisés en combinaison avec la mélamine triméthylolique (TMM) pour obtenir des propriétés ignifuges permanentes et améliorées. La dégradation et l'élimination du retardateur de flamme organophosphoré (MDPA) sur le tissu cellulosique ont été étudiées à l'aide d'un procédé d'oxydation avancé (AOP) basé sur la réaction de Fenton. La cinétique de dégradation de la MDPA dépend des concentrations en réactifs de Fenton (H_2O_2 et Fe^{2+} en milieu aqueux). Elle a été suivie en mesurant la demande chimique en oxygène (DCO) du mélange réactionnel. Dans les conditions optimales de dégradation, les propriétés mécaniques du tissu cellulosique après la réaction de Fenton restent inchangées dans le sens chaîne et de la trame du textile tissé. Le test d'inflammabilité et les résultats thermogravimétriques (TGA, DTG et PCFC) confirment la dégradation du retardateur de flamme MDPA du tissu.

Les espèces ignifuges étant dégradées et éliminées des textiles de coton, la valorisation énergétique par gazéification peut être effectuée pour augmenter le rendement énergétique en raison d'une meilleure combustion, mais aussi à cause de la composition du gaz de synthèse pendant la gazéification. Les résultats de gazéification montrent des propriétés de combustion accrues des textiles ignifuges après la dégradation et l'élimination des espèces ignifuges, qui permettent donc d'éco-concevoir la valorisation énergétique de ces textiles.

Pour confirmer et valider cette méthode écologique, une analyse de cycle de vie (ACV) a été réalisée pour analyser et évaluer les impacts environnementaux réels de cette nouvelle méthode de fin de vie des produits textiles ignifugés. L'ACV est l'une des principales méthodes d'évaluation pour effectuer l'évaluation environnementale des produits ou des services.

Les résultats de la combustion thermogravimétrique et de la pyrolyse confirment qu'il y a une libération de chaleur plus élevée après la dégradation de la réaction de Fenton. La libération de chaleur des textiles ignifugés de coton est augmentée de 51% après la dégradation des espèces ignifuges, ce qui rend le coton ignifuge dégradé intéressant pour la valorisation énergétique. La valorisation de l'énergie par des résultats de gazéification confirme qu'il y a bien une éco-conception en montrant des propriétés de combustion accrues des textiles ignifuges après la dégradation et l'élimination des espèces ignifuges. Enfin, les résultats de l'ACV ont montré des

valeurs d'impact réduites dans la plupart des catégories d'impact étudiées, en particulier dans le potentiel de réchauffement planétaire (GWP), l'acidification de l'air (AA) et dans d'autres catégories importantes en faveur de la dégradation et de l'élimination des espèces ignifuges des textiles assujettis à la gazéification.

Riassunto

La produzione, il consumo e lo smaltimento dei prodotti tessili hanno impatti negativi significativi sull'ambiente, in particolare tessili con ritardanti di fiamma finiture. I ritardanti di fiamma per i prodotti tessili sono stati ampiamente studiati per le loro fasi di sintesi e di produzione rispettosi dell'ambiente, ma al fine di prendere in considerazione un prodotto tessile ignifugo come, nella fase di fine vita eco-friendly sembra trascurato e ha bisogno di grande attenzione nel ciclo vitale. Tecnologie per la gestione dei rifiuti solidi sono in continuo miglioramento; discariche e inceneritori sono considerati come percorsi idonei per i rifiuti tessili, compresi i tessili tecnici. E' essenziale trovare modi diversi per valutare i metodi più ottimali o eco-progetti per lo smaltimento dei prodotti tessili.

La fase finale del ciclo di vita dei prodotti tessili ritardanti di fiamma è considerato come un ostacolo nel cessioni sostenibili correnti (discariche e incenerimento). La fine del ciclo di vita dei prodotti tessili ritardanti di fiamma a creare problemi, come ad esempio in discarica, c'è una possibilità enorme di specie ritardanti di fiamma o sostanza lisciviazione per l'ambiente. Allo stesso modo, specie ritardanti di fiamma diminuiscono rendimento energetico nel processo di incenerimento a causa di una combustione incompleta ed emette fumi tossici.

Specie ignifughi durevoli, per esempio, N-dimetil metilolo phosphonopropionamide (MDPA) è uno dei più efficaci ritardanti di fiamma organofosforici per tessuti cellulosici, utilizzati in combinazione con trimetilol melammina (TMM) per ottenere proprietà ignifughe resistenti e migliorate. Mentre il loro utilizzo è responsabile di gravi problemi di salute, e quindi vi è la necessità oggi di studiare i metodi per eliminare o degradare i prodotti ritardanti di fiamma durevoli che rimangono sui prodotti tessili scartato ritardanti di fiamma al termine della loro vita. Questo studio si espande e migliora la fase finale del ciclo di vita dei prodotti tessili ritardanti di fiamma, proponendo un eco-percorso e il trattamento prima della loro cessione. Un

eco-percorso si compone di degrado e la rimozione della specie ritardanti di fiamma o sostanza del prodotto tessile prima del suo smaltimento.

La degradazione e la mineralizzazione di un ritardante di fiamma organofosforico (MDPA) su tessuto cellulosico, è stata studiata utilizzando un processo di ossidazione avanzata (AOP) basato sulla reazione di Fenton. È stato valutato l'effetto di concentrazioni variabili di reagenti di Fenton (H_2O_2 e Fe^{2+} in mezzo acquoso) sulla degradazione del MDPA. La degradazione di MDPA in mezzi acquosi è stata monitorata misurando il COD (richiesta chimica di ossigeno) della miscela di reazione nel tempo. Le proprietà meccaniche del tessuto cellulosico dopo la reazione di Fenton erano inalterato in entrambe le direzioni di trama e ordito. I risultati dei test di infiammabilità e termogravimetria (TGA e DTG) hanno confermato la degradazione di MDPA del tessuto ignifugo. L'analisi PCFC (Pirolisi flusso di combustione calorimetro) conferma che, dopo la reazione di degradazione di Fenton, c'è un maggior rilascio di calore che rende il cotone trattato antifiamma interessante per una sua valorizzazione energetica.

L'obiettivo finale dello studio è quello di migliorare e potenziare la valorizzazione energetica dei prodotti di scarto trattati antifiamma, migliorando la resa energetica e ottimizzando la composizione del gas di sintesi durante la gassificazione.

Per convalidare la sostenibilità del progetto eco-compatibile proposto, è stata effettuata una valutazione del ciclo di vita (LCA) per analizzare gli impatti ambientali circa la fase finale del ciclo di vita dei prodotti tessili trattati antifiamma. L'LCA è uno dei principali metodi di valutazione per effettuare la valutazione di impatto generale per prodotti o servizi. Molti studi di LCA possono essere trovati per minimizzare gli impatti ambientali, cambiando i parametri tecnologici in fase di produzione e il comportamento dei consumatori nella fase di utilizzo di un prodotto tessile. Tuttavia, l'ottimizzazione dello smaltimento o nuove metodologie per la fase finale del ciclo di vita di un prodotto tessile è spesso trascurato o meno discusso. Questa tesi esplora possibili percorsi alternativi per il fine vita di prodotti tessili ignifughi. I risultati dell'analisi LCA hanno mostrato ridotti valori di impatto ambiente nella maggior parte delle categorie prese in considerazione, soprattutto nel potenziale di riscaldamento globale (GWP), acidificazione dell'aria (AA) e le altre principali categorie.

摘要

纺织品在生产, 消费和处理的过程中, 对环境都有着十分不利的影响。尤其是经过阻燃整理的纺织品, 其影响更甚。有关纺织品阻燃剂与环境的相关信息也较少。尽管生态友好型的纺织品阻燃剂在合成和生产阶段已经有着广泛的研究, 但是具有阻燃功能的生态友好型纺织品终期处理却被一直忽视, 这在产品生命周期中应该值得引起注意。随着固体废弃物处理技术的不断进步, 垃圾填埋和焚烧, 被认为是纺织品废弃物包括产业纺织品的最佳处理途径。在目前可持续的处理 (掩埋和焚烧) 阶段, 阻燃纺织品的终期处理一直被认为是一个难题。由阻燃纺织品终期处理产生许多问题, 例如填埋后, 阻燃剂有很大的可能迁移到环境中; 类似地, 阻燃剂由于不完全燃烧也降低了焚烧过程中的能量产率, 并且放出有毒烟雾。

基于此, 寻找纺织品废弃处理的生态方法是非常重要的。因此本文提出了一种对废弃阻燃纺织品最佳的生态处理方法。主要包括对耐久性阻燃纤维素纤维上阻燃剂在废弃处理前的降解或去除。煤气化处理 (而不是焚烧) 可以获得热稳定化, 探究去除阻燃剂前后纺织品的汽化能力。

作为棉织物最有效的一种有机含磷阻燃剂, N-羟甲基二甲基膦酰基丙酰胺 (MDPA), 当其与三羟甲基三聚氰胺 (TMM) 联合使用时, 可使棉织物获得耐久型阻燃效果。但与此同时, 也导致了严重的健康问题, 因此, 目前的研究重点应集中在找出可消除或降解在纺织品终期残留在织物上阻燃剂的方法。

本研究扩展和改善了阻燃纺织产品的生命终期阶段, 提出了一种在处置之前的生态路径和处理。即在终期处理之前从纺织品中降解和去除阻燃剂。其机理是, 基于Fenton反应的高级氧化方法 (AOP), 从而使纤维素织物上的有机磷阻燃剂 (MDPA) 降解和矿化。本文研究了不同浓度下的Fenton试剂 (水溶液环境下的 H_2O_2 和 Fe^{2+}) 对MDPA降解的影响。通过测量反应混合物随时间的变化的化学需氧量 (COD) 来监测水中MDPA的降解情况; 测量Fenton反应前后棉织物经向和纬向强力变化情况; 通过燃烧测试和热重测试 (TGA和DTG) 以及热解燃烧流量热量计 (PCFC) 测试, 证明MDPA阻燃剂在织物中发生降解。

阻燃剂从棉纺织品上降解和去除，可以产生更好的燃烧和气化期间潜在的合成气，从而可改善和增强废弃阻燃纺织品的能量增值。阻燃剂降解和去除后，纺织品更易燃烧，有利于产生可以利用的气体，从而达到了生态设计的目的。针对所提出的生态设计的可持续性验证，本文采用生命周期评估 (LCA) 来分析终期阻燃纺织品的生态设计对环境的影响。LCA 是用于产品或服务的总体评估的主要方法之一。

Fenton反应降解后通过热重和燃烧热解结果证实阻燃棉纺织品在阻燃剂降解后其热释放提高了51%，使得降解后的阻燃棉具有能源利用的意义。阻燃剂降解和去除后纺织品的燃烧性增强的气化结果，达到了生态设计的目的。

最后，LCA 结果显示，降解和去除纺织品上的阻燃剂以及气化过程，对全球变暖潜能值 (GWP)，空气酸化 (AA) 等指标的影响也是降低的。

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Eco-design for End-of-Life phase of Flame Retardant Textiles

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Lists of abbreviations

Advanced oxidation process	OH	Pyrolysis combustion flow
AOP	Life cycle assessment	calorimeter
Air acidification	LCA	PCFC
AA	Life cycle inventory	Raw Material Depletion
Air Toxicity	LCI	RMD
AT	Liquefied petroleum gas	Sodium hypophosphite
Ammonium phosphate	LPG	SHP
dibasic	Microscale combustion	Terrestrial Ecotoxicity
DAP	calorimetry	TE.
Ammonium polyphosphate	MCC	Thermogravimetric analysis
APP	Modified dimethylol	TGA
Butane tetra carboxylic acid	dihydroxy ethylene urea	Total heat release
BTCA	m-DMDHEU.	THR
Chemical oxygen demand	Municipal solid waste	Trimethylol melamine
COD	MSW	TMM
Derivative	n-methylol dimethyl	Tunable filter spectroscopy
thermogravimetric	phosphonopropionamide	TFS
DTG	MDPA	Water Depletion
dimethylol dihydroxy	Ozone Depletion Potential	WD
ethylene urea	ODP	Water Eutrophication
DMDHEU	Photochemical Ozone	WE
Flame retardant	Creation Potential	
FR	POCP	
Freshwater Ecotoxicity	Polybrominated diphenyl	
FWE	ethers	
Global Warming Potential	PBDS	
GWP	Polychlorinated biphenyls	
Hydroxyl radicals	PCB	

Chapter 1

Introduction and General Considerations

1.1 Flame retardants in textile industry

Textiles are an integral part of our daily lives. Other than apparel, woven, knitted, braided and nonwoven textiles are used in products such as curtains, coverings, bedding, furniture and medical furnishings, draperies, floor and wall coverings in various environments including healthcare centers such as hospitals. For decades flame retardants (FRs) have been used to increase the chances of survival against fire or flame by limiting its propagation. The total consumption of FRs in 2006 in Europe was estimated at 465,000 tons (EFRA, 2007) and the overall market for FRs in the Asia, Europe, and the United States in 2007 amounted to about 1.8 million metric tons (Defra, 2010). The estimated worldwide consumption of FRs is anticipated to reach 2.8 million tons by 2018 (ISI, 2015).

1.2 Flammability of textiles and consumer safety

Cotton is known as the king of the fibers for its comfort, being natural, environmentally friendly material and a renewable resource. Because of its good moisture adsorption and wicking properties, it is used commonly for the children's sleepwear, clothing, mattresses and home furnishings. Like most of the textile fibers, cotton has an extreme proneness to burning (Ramachandran et al., 2005). The flammable home furnishing textiles, for instance, curtains, beddings, table clothes etc., in the cases of fire can ignite easily and may lead to big fire development. These textile products are considered as the major fire hazards and are known as the primarily ignited materials.

According to a US statistics, over 3 million fire cases are reported every year and have resulted in 4500 deaths, 29000 injuries and 8 billion USD property losses (Alaee and Wenning, 2002), whereas, in Europe 2.0 – 2.5 million fire incidents are reported each year. In Europe, there are 20,000–25,000 deaths and 250,000–500,000 fire injuries each year (CTIF, 2006), among which 80% of the fatalities occur in private homes. In contrast to commercial buildings, the interiors of homes are full of easily ignited materials (textiles) and increase the chances of the fast fire spreading. Therefore, currently, the safety of humans and their assets has become an imperative issue due to the growing potential of flammable textile products. Textile industries, NGOs, and

Governments are extensively involved in investigating and developing different methods to prevent fires and their risks and effects (Bajaj, 2000).

1.3 Toxicity of flame retardants and sustainability

While FR textiles are essential in saving lives from fire, various FR chemicals have a long history of toxic issues. In 1979, the Polychlorinated biphenyls (PCBs) were banned in the United States when they were found to be the cause of cancer (Rogan et al., 1986). Like PCBs, the polybrominated diphenyl ethers (PBDEs) FRs were banned when it was discovered that they are able to accumulate in the wildlife and in people (breast milk) (Safe, 1994).

Figure 1 shows a typical life cycle of FR textile product. It is already known that each phase of the life cycle of a textile product, especially the production and use phases of textile products have substantial adverse impacts on the environment. A big amount of toxic emissions can be linked to the early stages of the textile life cycle, for instance, cultivation, fiber production, and pre-treatments (Allwood et al., 2006).

The use phase and end-of-life phases of textile products contribute greatly in generating toxic impacts. For instance, harmful chemicals may leached from clothes during wear or during launderings or during disposal in landfills at the end-of-life phase (Larsen et al., 2000).

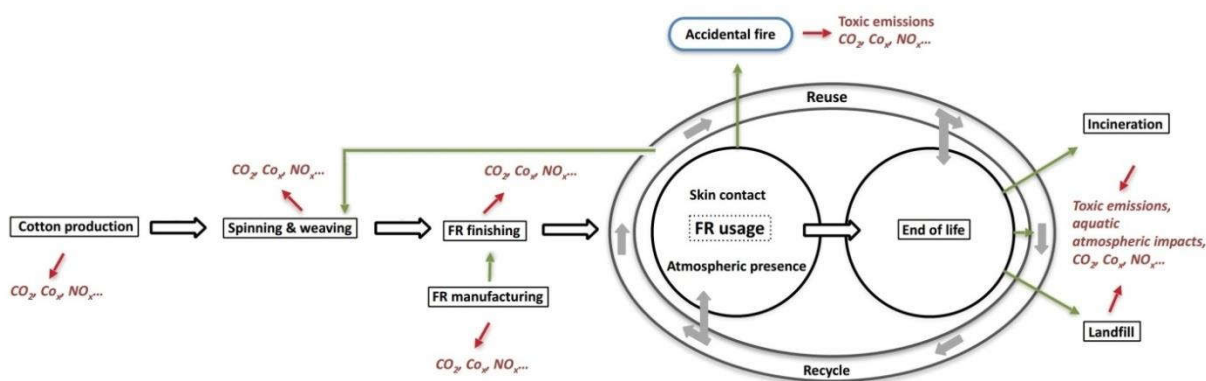


Figure 1. A typical life cycle of FR for cotton fabric (Paper I)

As like other industries such as building industry, the textile industry has responded stringently to the requirements of healthcare and fire safety. A great need and demand for fire safety and

healthcare organizations have moved the current textile industry to infuse resources and chemicals into the textile products which may harm the environment rather than protecting it (Julie et al., 2007). The requirement of lifelong attributes of FR textiles has also ended up in increased usage of chemicals. Indeed, many chemicals degrade by the exposure to some natural phenomena, for instance, light, microbial activity and they react with air or water. However commercially claimed FRs are yet to be found in the daily surrounding.

Scientific studies of FR products have been found to be the source of different environmental presences and pollution, for instance, air (Saito et al., 2007), dust (Stapleton et al., 2009), surface water (Rodil et al., 2012), drinking water (Bacaloni et al., 2007), and wastewater pollution (Meyer and Bester, 2004). An adequate amount of FRs has also been found in some fish species (Kim et al., 1986; Sundkvist et al., 2010) as well as in human breast milk (Kim et al., 1986). Meanwhile, many studies on the chemicals used to bring special fire safety and healthcare attributes to textiles have shown links to health effects from asthma to cancer (Julie et al., 2007).

Additionally, the persistence assessment of FR involves the occurrence of chemicals which are released to water, air and soil. Lots of people are exposed to FR textile products every day in homes and workplaces, including furniture, curtains, mattresses and even apparels. Additionally, most of the FRs are extremely persistent; they transfer easily from furnishings, appliances, and buildings into dust that eventually we breathe.

The information on the exposure of FR from textile products to environmental pathway is scarce. Unfortunately, the existence of FRs is neglected on a daily basis, in spite of risks induced with FRs during the exposure from household textiles by human contact through the skin, by inhalation and especially hand-to-mouth of substances emitted to the atmosphere during the lifetime of FR textiles.

Moreover, in a landfill the discarded FR textile products pose potential concern of leaching through the soil as the rainfall permeates underground and leads to surface and ground water toxicity (Marklund et al., 2005). On the other hand, the risks of toxic gas emissions during incineration are often neglected.

1.3.1 *Environmental impacts of flame retardants*

Critical or prolonged toxicity from the non-durable FRs occurs in leachable FR species and also due to dusting-off of a FR from products. In textiles, direct exposure of FRs to humans is conceivable through three major paths: dermal exposure, inhalation, and oral exposure.

Among various applications of non-durable based FRs in textiles, such as ammonium polyphosphate (APP) and red phosphorus, which have different mode of action, it is claimed that their application is considered as less problematic. However, the environmental impacts and toxicity to humans cannot be ignored (McPherson et al., 2004). Recent environmental studies on different FR products have shown great impacts on the environment. In a study, non-durable FRs such as ammonium phosphate appeared to have higher impacts on the environment. The results from those studies have shown the higher environmental impacts in many categories such as global warming, ozone layer depletion, human toxicity, marine and aquatic ecotoxicity, abiotic depletion and energy use (Petra et al., 2003; RedFR, 2011).

In another LCA study, ammonium phosphate dibasic (DAP) was found to be responsible for 60% of eutrophication in the production of latex (Jawjit et al., 2015). Moreover, the washed off DAP is a serious threat to the water system and soil. If left on the fabric and discarded for disposal (landfill or incineration) will emanate toxic gases increasing environmental impacts as mentioned earlier.

The durable FRs for textiles are reactive species, with commercial names such as, Proban CC, Pyrovatex CP, Aflammit P and KWB, and Flacavon WP. These durable FR species are organophosphorus compound N-methylol dimethyl phosphonopropion amide (MDPA) which are the most effective and durable FRs used for cotton and cotton/polyester blend fabrics (Kalliala and Talvenmaa, 2000; Ravichandran et al., 2011). They withstand a great number of launderings, dry cleanings or other cleaning procedures (van der Veen and de Boer, 2012). For improved flame retardancy and durability, MDPA is used with trimethylol melamine (TMM). There is a synergistic effect of nitrogen delivered by TMM in the occurrence of phosphorous

group (Weil and Levchik, 2008). Moreover, TMM increases bonding between MDPA and cotton fabric (Wu and Yang, 2006).

It is important to understand that both durable and non-durable FR textiles, leads at disposal phase, to leaching of FR if landfilled. Microbial decomposition of cellulosic materials (natural fibers) also enables the leaching of permanent FR in landfills. Though it is claimed that FR chemicals are degraded or destroyed by the exposure to some natural phenomena, such as light, microbial activity and react with air or water, the degradation process of FR compounds is certainly slower in cold climates. Accordingly, the risks associated with the exposure of low concentrations in ecosystems, for instance, small lakes or low flow rate streams and organisms in such ecosystems are greater in countries with cold climates than in warm climates (Marklund et al., 2005; Wargo et al., 2013). Therefore, it is important to consider end-of-life phase of FR treated textiles.

1.4 Research framework and thesis outline

1.4.1 Ecological issues and eco-designing of end-of-life phase

As the aforementioned associated toxicity of FRs, it is important to find alternatives and sustainable methodologies for the production, use and disposal phases of FR textile products. An ecological responsibility behavior leads to consider an appropriate end-of-life as an alternative to a landfill for FR textiles.

This thesis offers an alternative eco-designed disposal for FR textile products, for the natural fibers such as cotton. The schematic illustration of eco-design can be seen in Figure 2. The eco-design comprises of a prior degradation and removal of FR species to avoid leaching if landfilled and improve energy valorization of textile wastes in incineration or gasification process at the end-of-life phase.

Finally, a comprehensive LCA is used for the validation of eco-designed pathway with optimized disposal and end-of-life enhancements. More particularly, this scenario of end-of-life phase was compared to other alternative disposal pathways, such as incineration and landfill.

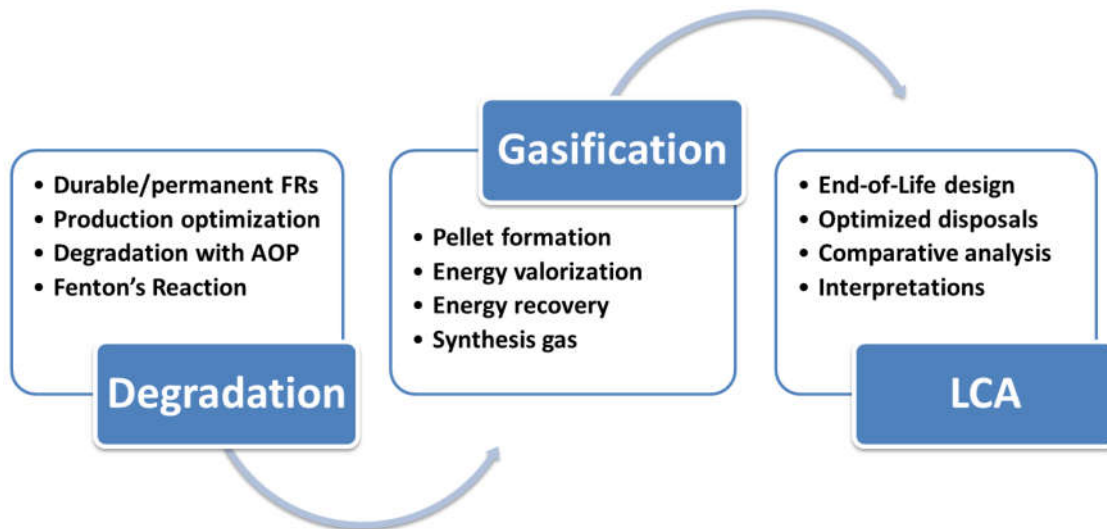


Figure 2. Eco-design for the FR textiles with optimized end-of-life phase

1.4.2 Degradation of flame retardant species

Improving the laundry durability using permanent FR, prevents its leaching from textiles during the use and disposal phases. However, today there is a need to study methods to eliminate or degrade durable FR products which stays on discarded textiles to increase the energy yields during the energy valorization by incineration or gasification. Meanwhile, an alternative valorization of FR cellulosic fabrics can be re-usability before ending into a landfill or incineration at the end of life, if the mechanical properties are still intact.

1.4.3 Energy valorization of FR textiles by gasification

Incineration is a novel approach for industrial textile waste by thermal valorization. However, along with a variety of benefits, it also produces other end-products, usually termed as polluting agents. Gasification is an eco-friendly solution to convert any carbon-containing material into synthesis gas (syngas).

In this PhD work, the thermal energetic yield by incineration was quantified by using laboratory experimental methods to assess thermal properties. For gasification of FR textiles, a custom-made pilot plant was used to quantify syngas composition and the energy yields. Compared to incineration, gasification process undertakes chemically reduced conditions, i.e.

with a great oxygen deficient environment. For that, gasification with energy yield and gas composition was carried out with and without prior FR degradation from textiles.

1.4.4 *Comprehensive LCA of the eco-design*

The end-of-life phases of textile products are often ignored or less discussed in LCA studies, especially in FR textiles. The main objective of this work is to provide an alternative end-of-life pathway for FR textiles. For that, a comparative cradle-to-grave LCA study was essential, to verify the environmental benefits of the eco-design compared to the usual disposals at the end-of-life of FR textiles.

1.5 Conclusions

Thus this Ph.D. will be separated into different chapters. Chapter 2 consists of a literature work on FR product used, on Fenton's reaction, which is an advanced oxidation process, on waste valorization by gasification as well as the LCA and environmental approaches. Chapter 3 will describe all the materials, techniques and experimental methods used for the study: the method used to prepare FR textiles as well as conditions used for getting optimal formulation for fixation and degrading the FR species using Fenton's reaction. The gasification method of the degraded FR textiles will be described, as well as the LCA methodology used for comparing the end-of-life of FR textiles. Chapter 4, 5 and 6 will give the results and general discussions on all experiments, on the degradation of FR textiles, on gasification of degraded FR textiles, as well as the environmental impacts of the proposed eco-design for end-of-life phase.

Chapter 2

Preliminary Bibliography

2.1 Theoretical Background of FRs

The FR substances were invented in between 1950 and 1980s, to facilitate the growing developments in the textile industry. The FR substances act with the involvement of one or more mechanisms of combustion: oxygen, heat, and fuel. Any FR works in resisting a material to undergo a gas phase reaction from the ignition or burning. The ignition or burning of a substance like a fabric exposed to a heating source undergoes into a temperature rise. The temperature of the heat source increases the net heat transfer rate of the fabric. Consequently the fabric undergoes a pyrolytic decomposition and starts burning. The end products of this fabric decomposition comprise of carbonaceous char, combustible and non-combustible gases. The heat generated during the burning of fabric is partly transferred to the fabric to withstand the burning process, while the rest of heat is lost to the surroundings (Horrocks, 1996).

The very aim of a FR system is to inhibit, resist or suppress the combustion process by interfering in any particular phase of the burning process, e.g. during ignition or fire spread, decomposition or even heating. FRs work in different methods to protect a material from the fire. For instance, bromine FR system works in interfering in burning reaction, which formulates a protecting layer and stops the flame. Halogenated FR systems inhibit the burning process by the production of combustible gasses. The phosphorous FR causes a material to generate char and prevents the pyrolysis process and consequently diminishes the flame.

2.2 Types and applications of FRs

To ensure the safety of the public, various fire standards, regulations and requirements are frequently discussed and improved accordingly. After successful safety tracks, a FR system is introduced to the particular product. Examples of FR systems applied to different products are mentioned in Table 1.

The field of technical protective applications is relatively large with differing requirements, as it comprises military applications and firefighters clothing. Undeniably, heat protective performance is required, additionally comfort and heat-moisture transfer properties, for instance, must be considered. Normally, technical protective fabrics contain up to four or five

layers, clothing for firefighters comprises of no less than four layers: external and internal covering, moisture fence layer and thermal liners. A fabric layer with effective FR is used as a thermal liner in firefighters clothing.

Table 1. Applications of FR in various sectors

Sectors	Applications
Transportations	Seat covers, seat fillings, armrests, headrests, textile carpets, curtains, ceilings, sidewalls, insulation panels, bumpers, stereo components, overhead compartments, and other computer systems.
Furnishing	Filling materials, foam upholstery, curtains, beddings, table clothes, fabric blinds and carpets etc.

A technical fabric structure, fire-blocker is often added during the wall constructions. Fire-blockers available are engineered textile products that use a combination of different fibers and fabric treatments. Another utilization of FR system is adaptable protection boards (thermal insulation) for building development. A noteworthy application of FR is in surgical curtains and blinds utilized as a part of operating rooms and air filters in the locomotive industry.

FRs have different chemical composition: indeed, they may contain halogens (bromine and chlorine), phosphorus, nitrogen, aluminum, magnesium, boron, antimony, molybdenum, or recently developed nano-fillers. The majority of FR textiles are classified as non/semi-durable and durable finished fabrics. Their durability is dependent on the binders used in pre-treatment finishes, or whether they are introduced into the fibers during spinning process. The non or semi-durable FRs find applications in the domestic sector, mostly in disposable medical gowns, curtains and carpets, upholstery, bedding and party costumes. On the other hand, inherently and durable FR textiles are used in high-performance applications (Horrocks, 1996).

The functionalization method may differ for natural compared to man-made fiber textiles. For instance, in polyester, FRs are added during melt-spinning, while in natural fibers FRs are applied by finishing wet processes. Moreover, FRs for cotton fibers, like phosphate or

phosphonate salts, are usually classified as non-durable and semi-durable FR, their durability property is dependent on the binders used in pre-treatment finishes. Non-durable FR finishes such as ammonium phosphates are mostly used in disposable medical gowns, curtains and carpets, upholstery, bedding and party costumes (Weil and Levchik, 2008). The phosphate based FR such as; ammonium phosphate dibasic (DAP) is highly water soluble as compared to ammonium polyphosphate (APP): both chemicals are commonly applied on cotton fabrics and can be removed easily after washing.

The durable or permanent properties for textiles are inherently added onto FR fibers to avoid leaching from the fibers, such as cotton, and it can be attained by an after-treatment. Although FR leaching is an issue, for cotton textiles chemically FR treatments are dependent on the formulation adherences or direct bonding to the fiber surface. For cotton fibers, durable FRs are used extensively; these FR are reactive species and are composed of organophosphorus and nitrogen-containing compound. Some well-known commercial FRs for cotton products with reactive species are Proban CC, Pyrovatex CP, Aflammit P and KWB, and Flacavon WP.

2.3 Production of FR textile

In the production phase of the FR cotton textiles during the finishing formulations, crosslinking agents are added to improve the flame retardancy and durability of the finish by developing a phosphorus-nitrogen synergistic effect (Uddin, 2013). The crosslinking agents for cotton are normally formaldehyde based, such as trimethylol melamine TMM and dimethylolurea (DMU) (Uddin, 2013). The treated cotton fabrics withstand a great number of launderings, dry cleanings or other cleaning procedures (van der Veen and de Boer, 2012). However, this finishing formulation is associated with the formaldehyde release (Bischof-Vukušić and Katović, 2012).

There is a big debate on the environmental impacts related to the use of the organophosphorus MPDA product as there is a high level of release of formaldehyde when MDPDA and TMM are combined (Mohsin et al., 2013). The release of formaldehyde from treated fabrics can cause mild to serious human health problems such as headaches, irritation of eyes or nose and skin rashes.

Most importantly, it has been classified as a cancer-causing substance (a human carcinogen) (Fowler et al., 1992; WHO, 2006). Indeed, researchers have tried to modify or develop new crosslinking reagents, such as low formaldehyde-content reagents or reagents with no formaldehyde in their structures. The modified dimethylol dihydroxy ethylene urea (m-DMDHEU) and the dimethylol dihydroxy ethylene urea (DMDHEU) reagents are widely used in the textile industry. Normally, these low formaldehyde-content reagents are compounds containing N-methylol group and yet the N-methylol compounds can release formaldehyde eventually. In the finishing process of FR to cotton fabrics, the N-methylol can react with hydroxyl groups of cellulose or with reactive N-H groups. These reactions end up in an undesirable loss of crosslinking reagents, and eventually from the N-methylol compounds, formaldehyde is released (tovarna ZVEZDA, 2002).

In literature, some formaldehyde alternative reagents such as a butane tetra carboxylic acid (BTCA) have been proposed. This is however, more expensive than formaldehyde reagents, has a limited laundry efficiency, and decreases the mechanical attributes of cotton fabric (Paul, 2014). Indeed, sodium hypophosphite (SHP) was found to be a more effective catalyst for cotton fabric when used with polycarboxylic acids (Clark and Andrewes, 1989).

At the present time, formaldehyde is yet preferably used in commercially available FR formulations, as it is cheap and extremely effective crosslinking reagent for cotton fabrics. Consequently, to cope with the impacts of formaldehyde on humans and the environment, there is a need to develop a formaldehyde-free formulation of finishes for cotton fabrics. Recent studies have brought some environment-friendly finishes for cotton fabrics, such as Chitosan phosphate (El-Shafei et al., 2015), enzymatic treatment (Wang et al., 2012), glycerol (Ferrero and Periolatto, 2012), α -hydroxycarbonyls (Meksi et al., 2012) and citric acid (Mohsin et al., 2013).

These environment-friendly finishes for cotton fabrics can solve the formaldehyde release problem; however, it requires a long set of experiments to achieve the desired results with limited information, particularly in formulations having numerous reagents or in the synergistic interactions. To overcome this problem, a formaldehyde-free crosslinking agent was used with the help of statistical tool to attain the optimized fixation to the cotton fabric. A FR formulation

with formaldehyde-free crosslinking agents, such as citric acid, sodium hypophosphite and phosphoric acid was utilized (Paper VI). However, to consider the real-case-scenario, the commercially available FR formulation having formaldehyde as a crosslinking agent was considered for the main research.

2.3.1 Optimization of FR fixation with statistical tools

Optimization of formulations for the FR systems for textiles can be attained by statistically designed experiments with several reagents additives within specific boundaries (Antia et al., 1982; Cullis et al., 1991). A statistical experimental design system can be used to optimize the performance of cotton fabrics treated with the FR reagents by predicting an effective concentration of finish fixation with minimum loss in mechanical properties. The commercially available FR and crosslinking agent (discussed in chapter 3, under section; FR product and additives) is permissible to get optimization information by using response surface methodology on reagent concentrations and mechanical properties of the cotton fabrics after the treatment.

2.3.2 Surface response methodology (Box-Behnken)

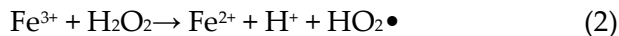
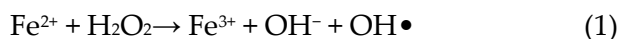
Response surface methodology is an empirical modelization technique devoted to the evaluation of the relationship to a set of controlled experimental factors and observed results (Annadurai and Sheeja, 1998). The methodology involves a model base knowledge achieved earlier; the data can be based on experimental outcomes or statistical knowledge.

2.4 Degradation and elimination via advanced oxidation process

Advanced oxidation processes are well known for their capacity to degrade and mineralize a wide range of organic compounds which are sometimes resistant to conventional biological oxidation. Many advanced oxidation processes, including Fenton (H_2O_2 , Fe^{2+}) and solar photo-Fenton processes (H_2O_2 , Fe^{2+} and solar irradiation) have proved to be useful in the degradation and mineralization of various organic toxicants and wastes (Xu et al., 2007) such as aromatic hydrocarbons (phenols, substituted phenols, chlorinated hydrocarbons, polycyclic aromatic), nitrogenous compounds and amines (Casero et al., 1997), and complex molecules like

pesticides, dyes, surfactants, pharmaceuticals, and mineral oils (Harimurti et al., 2010). Organophosphorus pesticide compounds have also been reported to be degraded by Fenton or Fenton-like reactions (Badawy et al., 2006).

Advanced oxidation processes are generally based on the generating reactions of short-lived hydroxyl radicals ($\text{OH}\bullet$) (Glaze et al., 1987), which are powerful oxidizing agents reacting with the majority of organic compounds by the second-order kinetics (Esplugas et al., 2002). Some other advanced oxidation processes use either hydrogen peroxide (H_2O_2) or ozone (O_3) source to generate oxidizing radicals such as hydroxyl $\text{OH}\bullet$ and hydroperoxyl $\text{O}_2\text{H}\bullet$. The $\text{OH}\bullet$ can be produced in-situ by various advanced oxidation process systems, for instance, chemical, electrochemical and/or photochemical reactions. It has been proved that these radicals have extremely high oxidation potentials: the $\text{OH}\bullet$ has a 2.8 V oxidation potential at pH 3 (Burbano et al., 2005). The major reactions for the generation of oxidizing radicals may be represented as;



In literature, it's rare to find studies reported on the degradation of organophosphorus FR compounds using the advanced oxidation processes such as Fenton's reagent, especially, in the domain of durable FR textiles. A part of this work, we proposed to study an in-situ degradation of organophosphorus FR MDPA from the cotton fabric in aqueous solution.

The degradation of MDPA in aqueous media can be monitored by measuring COD (chemical oxygen demand) of the reaction mixture over time. The degradation and mineralization from fabric were monitored by flame test and thermogravimetric analysis. In this study, we utilized an AOP for the removal of a durable organophosphorus FR from cotton fabrics, with a perspective of improving the energy yield of discarded FR cotton textiles during the combustion or possible re-usability.

2.5 FR waste valorization by gasification

Like all textiles, the FR textile products eventually become waste. Generally, such products are considered as municipal waste and are disposed-off via landfill or incineration. The incineration of FR textile products can generate various toxic compounds, including halogenated dioxins and furans depending on the FR species (John, 2013). The development of such compounds and their consequent release to the environment is due to incinerators operating conditions and its emission controls (Simonson, 2000). On the other hand, it would be interesting to see whether the FR textiles can be gasified or not, since FR resists the combustion.

Gasification is an intact breakdown of the biomass particles into a flammable gas, volatiles and ash in an encased reactor (gasifier) within the sight of any remotely provided oxidizing agent (air, O₂, H₂O, CO₂, and so forth) (Kumar et al., 2009). Gasification is a transitional step amongst burning and pyrolysis, which is a two-stage endothermic process. Within the initial step, the unstable parts of the fuel are vaporized at temperatures beneath 600°C by an arrangement of complex reactions responses. No oxygen is required in this period of the procedure (Curti, 2015).

Carbon monoxide, carbon dioxide, hydrocarbon gases, hydrogen, tar and water vapor are integrated into the unstable vapors. The by-products of the procedure, such as char (settled carbon) and slag are not vaporized. In the second step, char is gasified through the reactions with oxygen, steam, and hydrogen. A portion of the unburned char is combusted to discharge the heat required for the endothermic gasification reactions (Mann and Spath, 1997).

During the gasification process, a material (normally biomass) is burned in the presence of controlled oxygen, which yields synthetic gases as gaseous fuel. The gas is processed to make different chemical products or biodiesel. Consequently, gasification is a major environmental approach to attain biomass energy. The gasification process is dependent on certain operating parameters including gasification temperature, flow rates, oxidizing agents, feed type, properties, and design of the gasifier (Kumar et al., 2009).

Primary gasification products are gas, char, and tar. Gasification products, their creation, and some byproducts are emphatically affected by the gasification parameters, temperature, heat rate and fuel qualities. Vaporous items formed amid the gasification might be further utilized for heating or power generation (Pandey et al., 2015). The produced combustible gas during the gasification can be cleaned and utilized for the synthesis of unique chemical products or for the heat generation and additionally electricity.

Gasification is one of a technology that can even convert waste (from municipal solid waste (MSW) to agriculture or edit buildups, similar to coconut shells, rice husks, straw, wood deposits, bagasse, and so forth.) to a valuable and quality source for energy (Pandey et al., 2015). When dealing with complex disposals, gasification gives an upside of isolating the harmful substances from the fuel gas preceding the combustion.

In literature, studies utilizing LCA for investigating the waste to energy processes, focusing on incineration as a specific treatment can be found. Some of the studies are, integrated waste management system (Arena et al., 2003), a comparison performances of landfilling or mechanical treatment before combustion of solid recovered fuel (Finnveden et al., 2005). It would be interesting to compare environmental performance of landfilling, incineration and also gasification of FR textiles at their end-of-life.

2.6 LCA and environmental terminologies

In general, LCA is an environmental set of measures for gathering and inspecting the inputs and outputs of materials and energy and the related environmental impacts directly accountable for a product or system's whole life span. The LCA approach is described in four phases: (1) goal and scope definitions, (2) inventory analysis, (3) impact assessment, and (4) interpretation (Curran, 2006). A descriptive LCA framework can be seen in Figure 3. The LCA of any product, service or activity is mostly inventory-based, where raw materials, energy, and environmental emissions are distinguished later (Ison and Miller, 2000).

It should be noted that LCA analysis provides an enormous multidimensional set of input and output data that are difficult to interpret and comprehend. Additional precautions are generally

recommended while relating input to output data in the LCA product system to avoid uncertainties in impact analysis (Hermann et al., 2007). Moreover, LCA in general is conducted on two competing processes, in which a comparative analysis highlights the environmental benefits and drawbacks of one process over the other (Mann and Spath, 1997). Similarly, for a better understanding of the end-of-life phase of FR textile, LCA with comparative analysis was chosen.

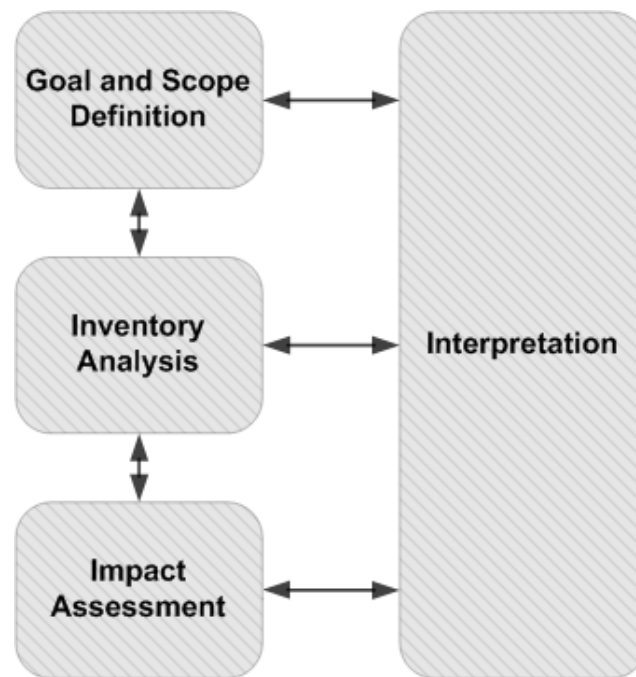


Figure 3. Illustrative diagram of four distinctive LCA phases

2.6.1 Components of LCA

For a standard LCA, four interdependent phases or components are carried out. The four phases of LCA are;

1. *Goal definition and scoping*

To identify the purpose of LCA and the expected product with determined boundaries including the assumptions based on the goals of the study.

2. *Life cycle inventory*

Quantification of the input raw materials and energy utilized while the production and their release into the environment at different stages.

3. *Impact analysis*

Assessment of the impacts on human health and environment derived from the inventory.

4. *Interpretations*

Evaluation of the opportunities to be considered, targeting the environmental impacts to be reduced by focusing on the energy use or evading the unnecessary process in the system.

2.6.2 *Cradle-to-grave and Cradle-to-gate variants*

The main variants involved in LCA are cradle-to-grave and cradle-to-gate. In the cradle-to-grave analysis, a comprehensive evaluation of all upstream and downstream energy inputs are considered and the associated environmental emissions of any item from production to disposal are interpreted. On the other hand, in cradle-to-gate LCA, the disposal phase is evaded. However, an LCA can be time-consuming and costly, consequently used with limitations for its use as analysis techniques.

2.7 **FR textiles and role of LCA**

The life cycle assessment (LCA) is a tool used to evaluate environmental impacts of a product permitting one to have comprehensive information on products' all life cycle stages and its environmental performance. A detailed study on emissions and alternatives of FR materials can be found in EU-funded project 'Life Cycle Assessment of Environment-Compatible Flame Retardants: Prototypical Case Study' (ENFIRO, 2009).

From ENFIRO, a phase sometimes with a smaller contribution to emissions could be the most important route of exposure. For instance, use phase of polymeric FRs have low impacts compared to their overall LCA scores, but the use phase found to be the main source of human toxicity and freshwater ecotoxicity emissions through wearing or abrasion and volatilization of

FR. Similarly, the emissions from the FRs end-of-life phase could be lower compared to the manufacturing or use phases but can have negative effects on the environment if not managed properly.

LCA has proven to be an environmental tool, liable for a comparison between waste management technologies and analyzing the related benefits and drawbacks (Fruergaard and Astrup, 2011). However, it is important to consider the literature data on fire emissions from FRs can be used if available. Detailed emissions should be included in LCA dependent on the FR type, e.g., CO, CO₂, HCN, NH₃, HCl, NO_x, HBr, VOC, PAHs, isocyanates, chlorinated, and brominated dioxins and furans for any brominated species. Similarly, if a product contains any specific additives along with the main species, it must be included in the measurement, for instance, the product containing brominated FR then the specific FR in question and brominated dioxins and furans should be considered (Simonson et al., 2005).

The interpretations of the environmental studies, however, portrait a diverse scenario where one fiber is a bad environmental choice in one case and the best in another (Nielsen and Schmidt, 2014). Similarly, environmental studies are carried out with certain system boundaries, which represent sometimes real or assumed situations for LCA outcomes (Conference Paper II). Furthermore, the use phase and end-of-life phase especially alternative end-of-life scenarios are not projected in LCA studies. A recent LCA study also shows that processes which are often ignored while conducting an LCA can have significant environmental impacts in that product's lifecycle (ENFIRO, 2009). Eluding processes in LCA with smaller impacts has created a huge gap in the literature by limiting the system boundaries, such as manipulating of end-of-life phases. This huge gap has also been discussed by numerous scientists, chemists, toxicologists, material scientists and fire safety researchers, commending to broaden the scope and system boundaries of the LCA studies by including unofficial or illegal scenario options (ENFIRO, 2009).

Moreover, there is a big debate on defining a suitable disposal for textile products over landfill and incineration, especially FR textiles. In many countries, incineration is not considered sustainable for a reason of generating emissions and ashes in the end. Additionally, FRs and

associated toxic gasses or fumes can also be released to the environment during inadvertent combustion of FR fabrics. Consequently, the landfill is undesirably adopted but is feared of landfill gas, leachate, and land shortage for the disposals, since every country will eventually run out of landfill space (Muthu, 2014). It was quickly concluded that a comparative analysis of end-of-life phase is urgently needed, especially when alternative disposal eco-designs or pathways are proposed.

Chapter 3

Materials and Methods

3.1 Flame retardant product and additives

MDPA FR (Aflammit KWB) and other resins including, TMM was provided by Thor, France; H₂O₂ (40% in aqueous solution) from Carlo Erba Reagents, France; FeSO₄.7H₂O, H₃PO₄, Na₂CO₃, and NaOH were obtained from Prolabo Chemicals, France. The reagents and chemicals were used as they were received. The properties of major FR components are given in Table 2.

Table 2. Properties of the FR and resins for bonding

Cas. Number	Name	Classification	Abbreviation	Melting point °C	Water solubility (mg/L) at 25°C	Vapor pressure (mm Hg) at 25°C	Log K _{ow}
20120-33-6	N-methylol dimethyl phosphonopropionamide	Durable FR	MDPA	84	1 × 10 ⁶	8.8 × 10 ⁻⁹	-1.68
51505-94-3	Trimethylol melamine	Fixing resin	TMM	170 ±5	-	-	-

MDPA FR (Aflammit KWB) and other resins including, formaldehyde crosslinking agent (Quecodur dm 70) and modified DHDMEU resin (Quecodur slf conc) was provided by Thor, France; sodium hypophosphite (NaPO₂H₂), phosphoric acid (H₃PO₄), sodium carbonate (Na₂CO₃), sodium hydroxide (NaOH) and citric acid (C₆H₈O₇) were obtained from Prolabo Chemicals, France. The reagents and chemicals were used as they were received.

3.2 Preparation of flame retardant textiles

3.2.1 Pad-dry-cure process

Pure cotton, dyed and plain woven fabric (170 g/m²) was used. All the samples were cut into 32 x 18 cm dimensions. The FR cotton samples were prepared by following the formulation instructions on the Thor (supplier) data sheet given. The FR was applied by the pad-dry-cure process, the other additives such as wetting agent, emulsifiers, and catalysts were used as recommended in the data sheet.

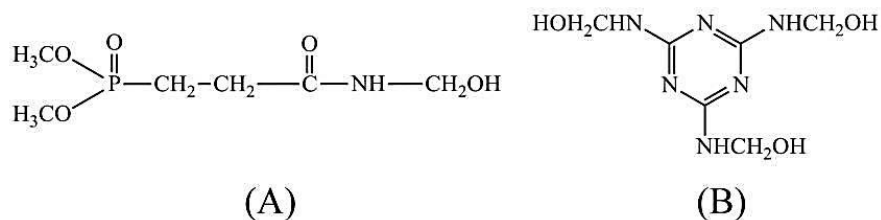


Figure 4. Structures of FR and other additives; (A) MDPA and (B) TMM

The drying and curing temperature were kept at 100 °C and 150 °C for 4–5 minutes respectively. Neutralization of finished cellulosic fabrics is carried out with an alkaline bath using Na₂CO₃, to remove residues and neutralize the effects of acid used as a catalyst. The chemical structures of targeted FR compounds in aqueous solution are shown in the schematic illustrations, Figure 4.

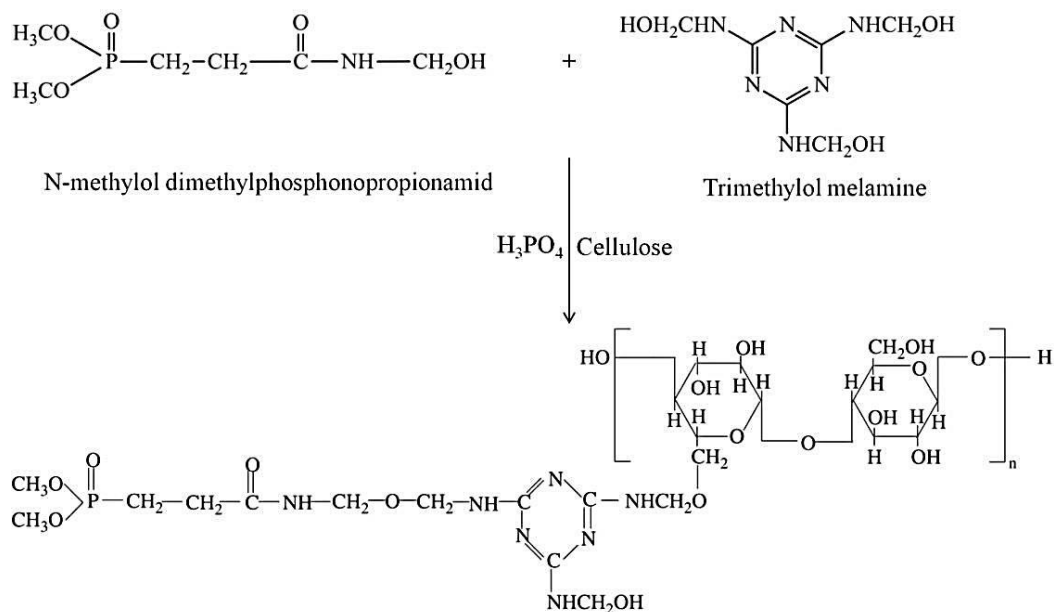


Figure 5. Scheme of MDPA bonding with cotton assisted by TMM under acid-catalyzed conditions

MDPA which has a methylol group is capable of making an ‘aminal’ bond with cellulose in the absence of other additives at approximately 52% without cross-linking in acid-catalyzed conditions (Wu and Yang, 2006). The use of TMM increases cellulose bonding with MDPA, and it also increases the flame retardancy of the treated fabric (Wu and Yang, 2007). TMM is likely to

self-condense, forming an insoluble polymeric water network on the cellulosic fabric. It creates a nitrogen-phosphorus synergistic effect, which enhances flame retardancy (Schindler and Hauser, 2004). The schematic illustration of MDPA bonding to cellulose by TMM can be seen in Figure 5.

3.2.1 Optimization of flame retardant finishing

As aforementioned (Section: 2.3.1. Production optimization with statistical tools), the statistical experimental design system was used to optimize the FR finishing on the textiles. Here, the aim was to have a formulation, which gives optimized FR properties and low mechanical loss to the fabric. A statistical tool, the response surface methodology gave empirical formulae to optimize/enhance the required parameters.

For an overall view, with the lowest concentration of commercially available formulation, the flammability of FR cotton fabric treated, (Aflammit KWB: 200 g/l; Quecodur dm 70: 25 g/l; Quecodur slf conc: 10 g/l; phosphoric acid: 22.5 g/l) was reduced to 6.8% from 100%. With the highest concentration (Aflammit KWB: 500 g/l; Quecodur dm 70: 25 g/l; Quecodur slf conc: 80; phosphoric acid: 22.5 g/l), FR treated cotton fabric lost mechanical properties with 40% loss in elongation and 16.05% loss in tensile strength. The drastic change in mechanical properties can be controlled by attaining optimal formulation of concentrations statistically. The model was found adequate and the optimal formulation for the output response parameters with reduced damaged area and improved mechanical properties of the FR cotton fabrics, were determined (Paper V).

3.2.2 Validation of optimized production parameters

FR fixation on the cotton textile needs certain parameters to be achieved for an optimal formulation that includes specific reagent concentrations (cross-linkers and FRs), suitable curing and drying temperatures, pick up rate and reaction conditions. To have that optimal formulation a statistical tool was used to avoid long set of experiments with better FR properties and lower mechanical loss to the fabric.

The optimal concentration for the FR formulation was analyzed from the numerical optimization approaches with the software Design-Expert version 7.0.0 (StatEase) and is shown in Table 3. Since the aim of this methodology was to get the optimal concentration for the FR cotton fabric with minimum flammability and maximum mechanical properties. The formulation with concentrations of Aflammit KWB [296 g/l], quecodur dm 70 [40 g/l], quecodur slf [56 g/l] and phosphoric acid [25 g/l] ought to give the optimal results, dependent on desired parameters. In order to verify the suitability of the model empirical equations, verification experiment was carried out for the formulation under the adjusted optimal concentrations.

Table 3. Optimized formulation for commercially available FR for cotton (Paper V)

For individual parameters	Aflammit KWB [g/l]	Quecodur dm 70 [g/l]	Quecodur slf conc [g/l]	Phosphoric acid [g/l]	Predicted values	Actual values
Damaged area (cm ²)	499.97	34.62	19.26	20.00	5.68 (cm ²)	6 (cm ²)
Elongation (%)	200.00	23.32	28.06	22.80	9.29 (%)	9.15 (%)
Tensile strength (N)	200.00	23.48	29.60	22.61	345.97 (N)	345 (N)
For combined parameters						
Optimized damaged area, elongation and tensile strength	295.89	40.00	55.99	25.00	11.35 (cm ²), 8.98 (%) and 333.27 (N)	12 (cm ²), 8.8 (%) and 331 (N)

The associated experimental and predicted values were compared and the percentage errors were calculated to be 5.41% for damaged area, 2.04% for elongation and 0.68% for tensile strength, in the FR formulation. The marginal difference between the predicted and actual results is within permissible limits indicating the formulations obtained by response surface methodology were practical (Paper V).

3.3 Degradation of flame retardant species

The degradation of the durable FR MDPA for cotton was carried out both, in the aqueous solution and as well as in bounded state on cotton fabric (*in-situ*). Degradation of FR species in

aqueous solution was carried out with one concentration (2 g/l of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and 6 g/l of H_2O_2), to find the ability of Fenton's reagents to degrade the durable FR and other additives.

Since, the aim of this research to degrade FR from cotton textile, various parameters were considered to find optimum FR degradation and low mechanical loss to fabric. For in-situ degradation of FR from cotton fabric, three different concentrations of Fenton's reagents were used: 100, 200 and 500, mg/l of the ferrous source ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$), while the quantity of hydrogen peroxide catalyst (H_2O_2 -98% in aqueous solution) was kept constant at 1 g/l.

3.3.1 *Degradation of flame retardant in aqueous form*

Before testing the *in-situ* degradation of FR on cotton fabric degradation, the degradation of the targeted FR MDPA in a free state (in the aqueous solution 400 g/l) by Fenton's reagents, was studied using $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (2 g/l) and H_2O_2 (6 g/l). The degradation of FR with respect to time was monitored by analyzing the reduction in COD (Chemical oxygen demand) values.

3.3.2 *In situ degradation of flame retardant on cotton fabric*

The degradation of FR from cotton fabrics was carried using Fenton's reagents in a 2 liter Erlenmeyer flask using a magnetic stirrer. Different concentrations of Fenton's reagents were used: 3 different concentrations of the ferrous source were used: 100, 200 and 500, mg/l, while the quantity of hydrogen peroxide catalyst was kept constant at 1 g/l. Indeed, previous studies have demonstrated that organic degradation is nearly the same for increasing the H_2O_2 concentrations (Zhang et al., 2006). Therefore, only the concentration of ferrous ions was varied in this study. The flask was covered with an aluminum foil to avoid any interference of light in the Fenton's reaction.

After the Fenton's reaction, all fabric samples were soaked for twenty minutes in a 40 g/l of NaOH solution to stop or quench the Fenton's reaction (Pontes et al., 2010). The COD reduction values were analyzed for the first time with in-situ degradation of FR from the cotton fabric. Since COD analysis with a physical fabric was carried out for the first time and considering the sensitivity of COD calculations, general standards were evaded for preliminary understandings.

3.4 Characterization methods for degradation

FR treated cotton fabrics were analyzed before and after degradation with Fenton's reaction using the flame test, TGA (Thermogravimetric analysis), PCFC (Pyrolysis combustion flow calorimeter), and a fabric tensile strength tester.

3.4.1 Consumption of oxygen for oxidation (COD)

The COD (consumption of oxygen required for oxidation) allows to calculate the mass of oxidized organic materials and hence the concentration of organics in the reaction solution (Gerike, 1984). Indeed, oxidation of organic materials in the reaction solution results in the production of inorganic but stable compounds such as carbon dioxide and water. To have a preliminary understanding of degradation, theoretical COD as a base of the FR on fabric sample was calculated. Initially the base COD value was set to (422 mg/l) per sample, while the COD reduction was carried out experimentally in different interval of times during the Fenton's reaction. COD of the Fenton's reaction mixture containing FR MDPA and FR treated cotton was analyzed using Hach COD vials (Hach, Germany) and was measured with a Cecil CE3020 UV/VIS scanning single beam spectrophotometer (Cecil, UK).

3.4.2 Thermogravimetric analysis (TGA)

TGA was carried out using Thermogravimetric Analyzer TGA 2950, TA Instruments, US. TGA was performed in an open platinum sample pan and the measurement was conducted in nitrogen. The samples were heated from 30 to 500 °C at a constant heating rate of 10 °C/min under nitrogen atmosphere (flow rate: 100 ml/min). The samples weighing between 5 (± 4) mg were used. A derivative thermogravimetric (DTG) curve was used to determine the most apparent point of the weight loss.

3.4.3 Pyrolysis combustion flow calorimeter (PCFC)

PCFC tests were performed using Microscale combustion calorimetry (MCC), FAA Micro Calorimeter, Fire Testing Technology, East Grinstead, UK, according to the standards ASTM D7309 (ASTM, 2007). Samples weighting of 4.7 (± 3) mg was heated under nitrogen flow, in the presence of N₂/O₂: 80/20 flow gasses are extracted and sent to a combustion chamber. The

detailed instructions on PCFC constructions are discussed elsewhere (Lyon and Walters, 2004). All samples were measured at least three times with ± 4 % reproducibility.

3.4.4 Mechanical properties

After Fenton reactions, the mechanical properties were tested to check the fabric strength by using MTS (2/M) testing system. The tensile strength of each cotton sample was determined by repeating the test at least 5 times for each sample according to French norm test procedure (NF EN ISO-13934-1, 2013). The samples were cut in 30 x 5 cm length by width for the determination of tensile strength, the test was carried out in the warp and weft directions five times each. The average values were taken. Threads were removed equally from each of the long edges till the width of the sample is obtained.

3.4.5 Flame test

The classification method based for assessing the burning behavior of textiles was carried out on cut samples (150 x 300 mm) according to French standard (NF-G 07-113, 1972). A specimen fabric is fixed and from bottom center flame is introduced. Measurement of the specimen is calculated in area length (cm²) of the damaged surface. The classifications of flame testing measurements can be seen in Table 4.

Table 4. FR classifications according to French standard norms

Classes	Surface of damaged area
A	Up to 10 cm ²
B	10-40 cm ²
C	40-100 cm ² edge must not be reached
D	100-200 cm ² or below 100 cm ² if the edge has been reached
E	Above 200 cm ²

3.5 Gasification of FR textile

In gasification, a biomass is burned in the presence of controlled oxygen, yields a synthetic gas as gaseous fuel. The produced gas can be processed to make different chemical products or biodiesel. Consequently, gasification is a major environmental approach to utilizing biomass

energy. The process is dependent on certain operating parameters including the gasification temperature, flow rates of feed, oxidizing agents, feed type and its properties, and type and design of the gasifier. Gasifiers are classified on types of bed and flow, while the gasifier beds are either fixed bed or fluidized bed. Whereas, the spouted bed gasifiers are special case of fluidization and have demonstrated various advantages, for instance relatively lower gas flow rates, can handle coarser solid particles and especially the segregation is barred by a peculiar hydraulic structure (Curti, 2015).

3.5.1 Spouted bed gasifier

A prototype spouted bed pilot gasification unit was utilized, which can be operated to produce and analyze syngas. This unit is equipped with an in-line gas analyzer. Its scheme is represented in Figure 6. The gasification unit is based on a square based spouted bed having 200 mm thick sides. A preheated spouting gas is generated in a burner where water is sprayed into the combustion gas, liquefied petroleum gas (LPG) to reach a suitable steam concentration, upon requirement.

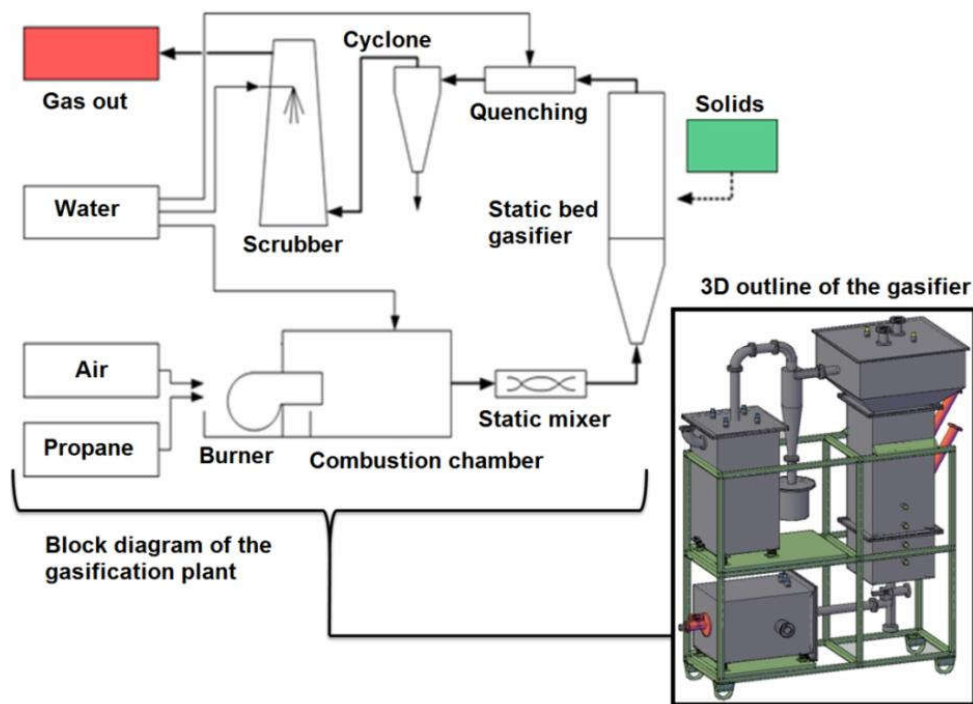


Figure 6. Schematic illustration of the customized spouted bed gasifier with 3D and block diagram (Paper IV)

Downstream of spouting, the gasification product is cleaned from powders in a cyclone, followed by a water scrubber for cooling and absorbing soluble acid components. The reacting pellets are prepared off-line with hands, were stored in an upper bin, continuously metered and introduced in the spouted bed reacting zone from the side openings. Nevertheless, various configurations such as standard spouting and spouting with secondary fluidization were considered with the insertion of a draft tube as an additional internal support. The auxiliary fluidization is expected to provide advantages for larger units in terms of reaction control (Curti, 2015).

3.5.2 Preliminary pellet preparation

Indeed, spouted bed gasifier improves the uniform distribution of feed particles; however, overfeeding can lead to plugging and reduced conversions efficiencies while starve feeding leads to fewer gas yields (Kumar et al., 2009). Therefore, an optimum feed rate is required for an effective gasification system. Generally, disposed textile waste is processed in bulk without any modifications and is incinerated as it is received basis. For lab scale, initially, pellets of FR treated cotton fabric were prepared in order to find the optimum conditions for the gasification. Considering pellets for the industrial scale, equipment capable of producing large lots of particles from industrial textile waste can be used. Larger units can also process textile scraps or fragments having a nominal size of a few centimeters.

On the preliminary basis, following steps were taken for textile pellets. The starch solution was prepared by adding 10-15 g of sizing agent (maize starch) into 1 L of water, for the cotton fabric to be transformed into pellets. The solution of water and starch was heated at 100 °C with continuous stirring till the sizing solution went from translucent to clear and thickens in consistency. The starch solution was kept to cool down at room temperature. The fabric samples were dipped in the sizing solution and gently pressed while rolling to squeeze out the excessive size solution from the fabric with both hands (Figure 7B). For the cotton fabric to be in rolled form, the fabric rolls were then oven-dried for 30 minutes at 60 °C.

The dried cotton fabric rolls were cut into 1 cm in length, suitable to be fed into customized gasifier. The prepared fabric pellets (Figure 7C) were used for the gasification process. The prepared textile pellets were transferred to the hopper of the gasification unit. The feeding of textile pellets to the gasifier was maintained at the rate of 150 g/min. Reaching the gasification temperature (>700 °C) with continuous feeding, the produced gas can be analyzed by a syngas analyzer.

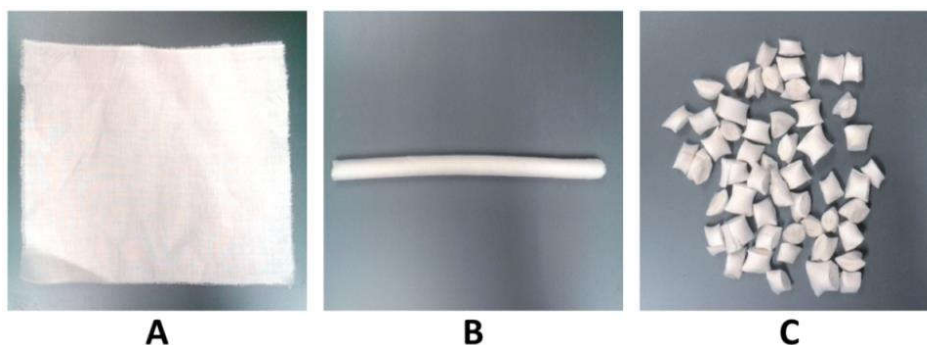


Figure 7. Handmade pellets of the cotton fabric to be fed into the gasifier. A) Plain cotton fabric, B) dipped in starched and rolled fabric and C) cotton fabric cut into pellets (Paper IV)

3.5.3 Gasification of flame retardant textiles after degradation

The prepared textile pellets after the degradation of FR substance were examined for the gasification. To have optimum gasification of the pellets, it's important to consider various pre-operation parameters. For instance, a consistent temperature inside the reactor and continuous pellet feed rate. Initially, the gasifier unit was set to achieve a regular temperature.

3.5.4 Temperature control in the rig

Detailed illustration of variant temperature controls with thermocouples can be seen in Figure 8. Before performing the gasification process which occurs at a high temperature, the refractory was conditioned in order to evade any thermal fractures. For that temperature is increased gradually to remove the excessive water or humidity present in the matrix. Such operation requires some hours to reach stability. Details on a gradual increase in temperature in different areas of the experimental unit are discussed in section 5.2.1 (Thermal transitory analysis).

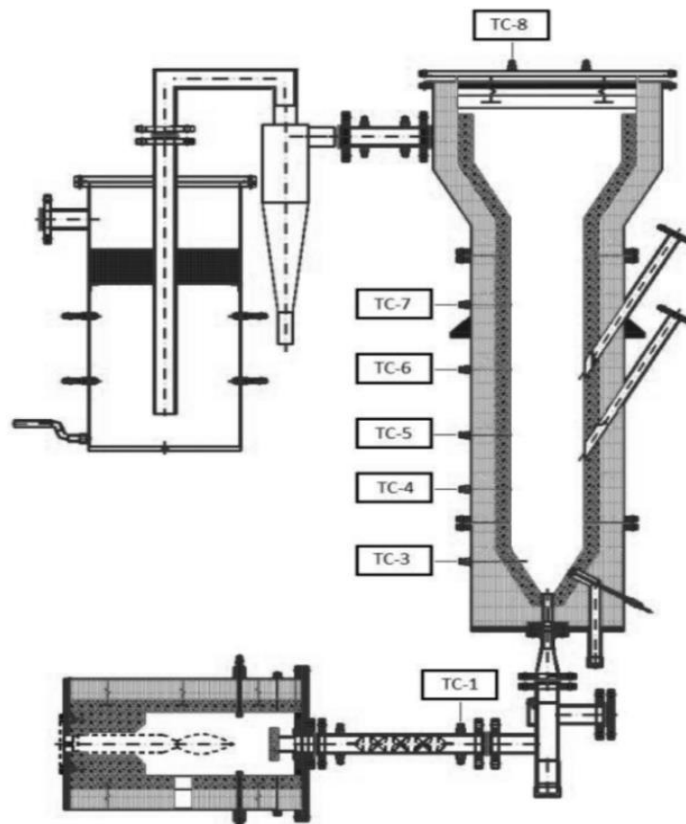


Figure 8. Thermocouples in the gasifier reactor (adopted from Curti, 2015). Here TC1 is a static mixer, TC3 and TC4 are the base of the reactor, TC5, TC6, and TC7 are mid sections of the reactor, and TC8 is the top

In the preliminary test, the burner was set at 11 kW power with an excess of air ($\lambda=1.2$), water was not added in the combustion chamber. During this preliminary test, the reactor was kept empty in order to remove water. The first increase in temperature is between TC-1 and the others thermocouples, which is linked to the slowness of the concrete to reach the equilibrium temperature. TC-1 is downstream to the static mixer and TC-3 is top of the gas inlet.

3.6 Characterization methods for gasification

3.6.1 Pellet flow rate and thermal transitory analysis

In gasification, the transitory thermal analyses require a primary temperature and time duration and are one of significant parameters for the quality and composition of the produced gas during the gasification.

It is important to analyze the variation of temperature distribution over time to have thermal transitory leading to a temperature suitable for the gasification to produce syngas. A preliminary gasification state with an optimum flow rate of prepared pellets to reach a temperature above 800 °C inside the reactor was analyzed.

3.6.2 Syngas analysis

The gas produced during the continuous thermal process of gasification may vary in composition. There can be different factors associated with the change, for instance, the reactor temperature, the inlet gas composition and the quality of the waste. A medium can be utilized to decide the integrity of the process; in any case, it can be dubious to decide since it has not been conceivable to organize a gas-chromatography contraption close to the model unit.

The likelihood to stock the gas in sacks to analyze later was not taken into consideration, since some substantial hydrocarbons may condensate or adsorb amid carriage, conceding the last outcomes. However, a tunable filter spectroscopy (TFS) was chosen to analyze the continuously produced syngas. The schematic illustration of TFS spectroscopy can be seen in Figure 9.

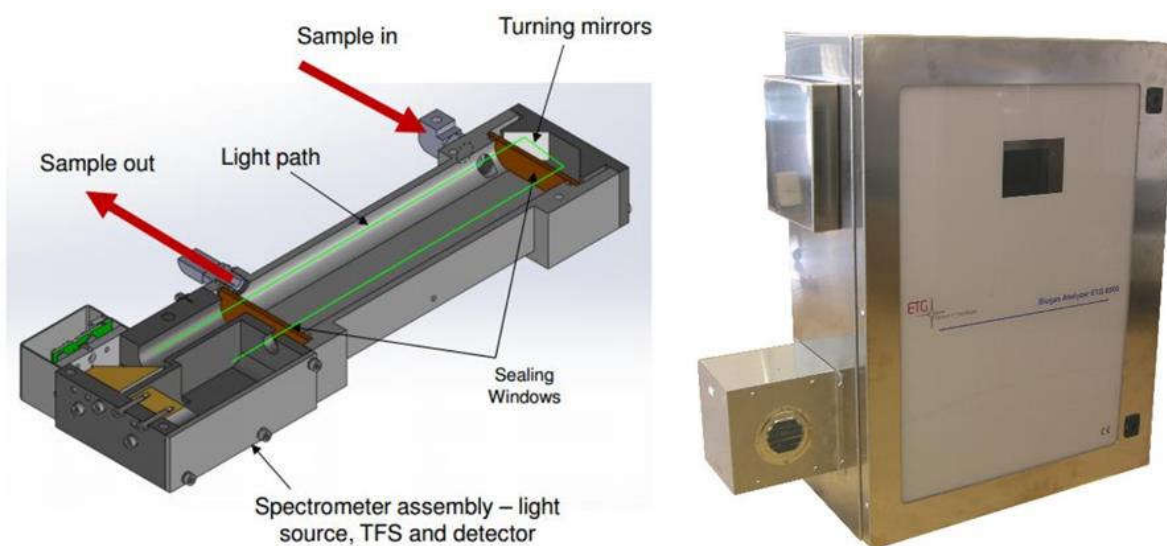


Figure 9. Schematic illustration of on-line syngas analyzer with the principle of operation (adapted from Curti, 2015)

3.6.2.1 Principles of syngas analyzer (Tunable Filter Spectroscope)

The TFS analyzer is a non-contact, light absorption based gas analyzer equipped for ppm to percent level fixation checking of numerous gas mixes. The analyzer comprises of a light spectrometer, a flow-through specimen cell, a solitary component photo-detector, and the supporting gadgets. The spectrometer furnishes wavelength examining with high optical throughput. An advanced spectral preparing calculation processed in the implanted hardware gives profoundly exact and robust quantitative estimations. The TFS gas analyzer is arranged and adjusted for a particular wavelength examination locale relying upon the application for which it is proposed. It is intended to be a committed on-line checking framework.

The assimilation or absorption spectrum range of every compound is exclusive which goes about as a "finger impression" for recognition. The magnitude of the ingestion is an element of gas atoms quality. With a known way length, weight, and temperature, the magnitude of the ingestion spectra are then used to compute volumetric concentrations.

The TFS Gas Analyzer utilizes an inner weight transducer to quantify the example weight progressively empowering weight variation adjustments. The flow cell is warmed to a steady temperature (default esteem is 60 °C) with a specimen preheat module to keep up both example and optical sensor temperature at a consistently aligned temperature, in this manner guaranteeing estimation precision and security in spite of test and ecological varieties.

This technology permits constant examination since it is conceivable to get the gas compositions every 5 seconds. The non-contact between the gas and the identifier maintains a strategic distance from sensor harming. Some extra sheets introduced on the analyzer, permit deciding the amount of H₂ and O₂ in the gas outlet. The latter is specific critical for all the agent stages since the presence of oxygen in the liquid is a key point on the exhibitions of the thermal responses.

3.7 Comprehensive LCA of flame retardant textile

LCA has been performed as a cradle-to-grave analysis focusing the end-of-life phase by applying the proposed eco-design and pathway of FR textile products prior to its disposal. The

proposed eco-design consists of degradation and removal of the FR substance from the textile product. Later on, the textile product is incinerated, landfilled and gasified to verify the advantages of degradation and removal of FR substance. The LCA was carried out according to ISO 14040 (ISO14040, 2006a) and ISO 14044 (ISO14044, 2006b) standards. EIME software (Bureau Veritas, CODDE) was used.

3.7.1 Functional unit and system boundaries

The functional unit was 1 kg curtain having plain woven, dyed cotton fabric and treated with organophosphorus FR, washed 25 times during lifespan of 10 years. The geographical scope was chosen to be Turkey for the manufacturing of FR cotton curtains, while Italy for the use and disposal phases. Figure 10 shows a typical life cycle for the FR cotton curtain that combined manufacturing of cotton fabric first and treatment of FR and finally curtain manufacturing. All the important processes in the life cycle of the FR cotton curtain are included (cradle-to-grave).

The system boundaries of this study were set at three different disposals at the end-of-life phase; first usual landfill, second incineration and third the gasification. In the proposed eco-design, there is removal and degradation of FR substance from the fabric which then goes through landfill, incineration, or gasification. The potential environmental loads and benefits of the incineration and gasification of FR curtains are included as the cutoff values since incineration with energy recovery was considered.

Transport (interdepartmental, local and international) involved in the life cycle of the FR cotton curtain from raw material to finished product and transport of used curtain to incineration plant is added in this study. The inventory data for the distribution of cotton curtain is calculated based on average distance of 1000 km travelled by lorry truck with 17.3 t capacity. According to a semi-structured questionnaire, cotton curtains are washed 20-25 times in 10 years of life span.

Hence, we assumed that the cotton curtain is washed, tumble-dried, and ironed 25 times. Water, energy, and detergent consumption over the lifetime of a cotton curtain that corresponds to 25 washes before disposal is considered with assumptions; 60 °C wash in an automatic washing

machine, the laundry mass load, amount detergent etc. are adjusted accordingly. The fraction of FR released during washing or use phase is omitted in this study.

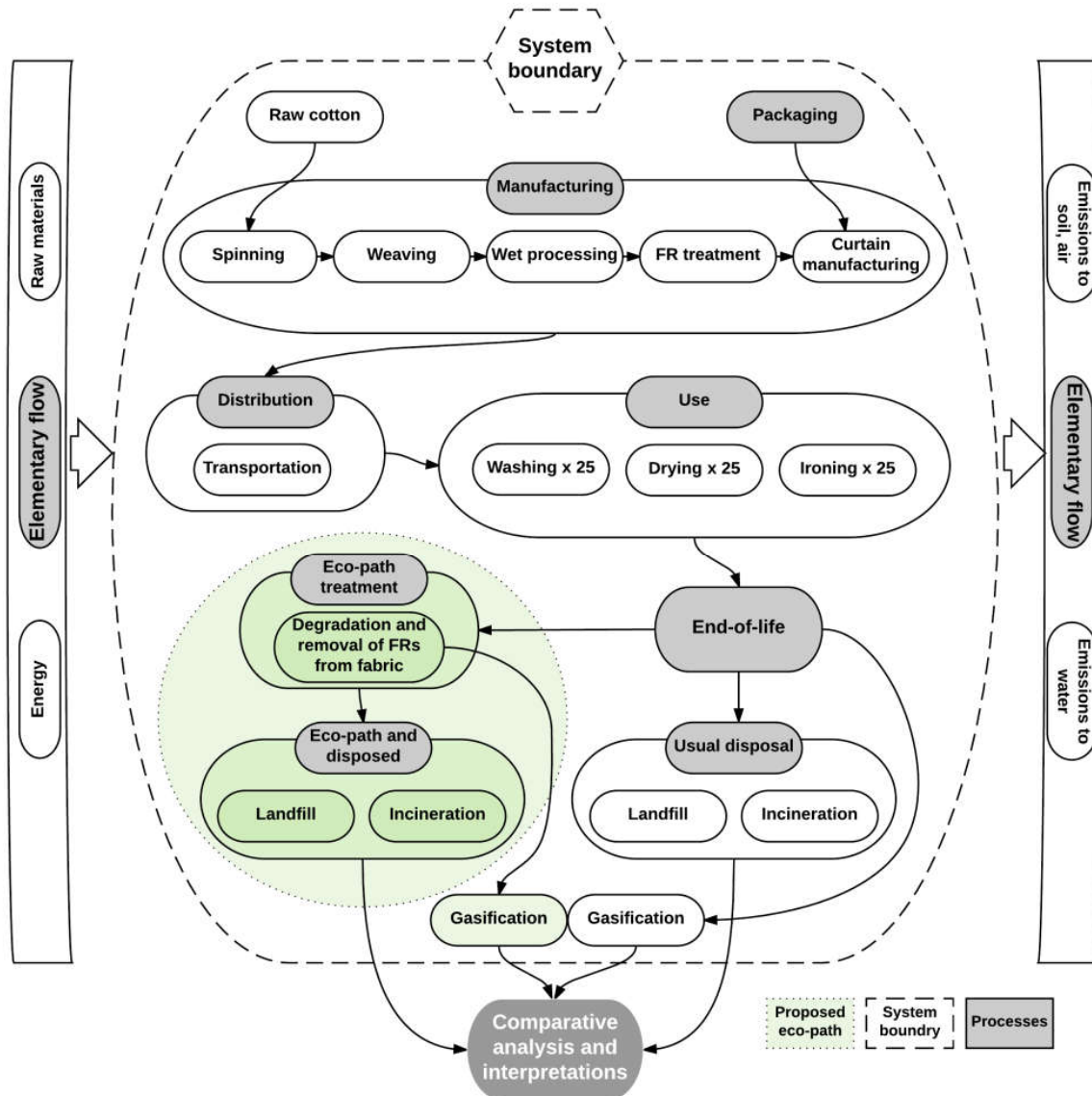


Figure 10. The life cycle and system boundaries of the FR cotton curtain with proposed eco-design at the end-of-life

3.7.2 Life cycle inventory (LCI) and comparative analysis

Life cycle inventory analysis was demonstrated using EIME software provided by Bureau Veritas CODDE (France). EIME software calculates LCI values using databases such as ELCD,

Eco-Invent and CODDE. Consumption of raw materials, electricity, and steam for these processes are estimated from pre-defined parameters in EIME software (CODDE) and available data related to cotton processing in the literature (Baydar et al., 2015; Koç and Kaplan, 2007; Kooistra et al., 2006; Yilmaz et al., 2005). For simplification, LCI inputs of the cotton curtain with FR processing are mentioned in Table 5.

Table 5. Inventory data for FR processing of cotton curtain per functional unit taken as the reference scenario

Material inputs	Units	Consumption per functional unit
Caustic soda	kg	3.00E-02
Chelating agent	kg	2.40E-02
Desizing agent	kg	3.55E-03
Dyeing agent	kg	4.88E-02
Electricity	MJ	3.12E+00
Flame retardant and resins	kg	3.20E-01
Formic acid	kg	4.70E-02
Hydrogen peroxide	kg	3.00E-02
Lubricant remover	kg	6.00E-03
Lubricating agents	kg	1.50E-02
Peroxide stabilizer	kg	1.20E-02
Salts	kg	8.30E-01
Silicone softener	kg	1.50E-02
Soap/detergent	kg	1.50E-02
Sodium carbonate	kg	2.56E-01
Sodium thiosulphate	kg	1.50E-02
Soft water	L	1.80E+02
Steam	MJ	2.68E+01
Wetting agent	kg	1.10E-02

3.7.3 End-of-life scenario building

A characterization analysis was applied on the proposed eco-design, for which six different scenarios were performed to identify the possible applications at the end-of-life of FR cotton textiles. Three scenarios were chosen as reference cases, incineration, landfill, gasification and subsequently, additional three cases of incineration, landfill and gasification but with applied eco-designs were considered in order to assess the environmental improvements of the process. A brief description of studied scenarios is given in Table 6. All of the scenarios in Table 6 have a

common life cycle of FR cotton fabrics, which starts from the raw cotton and ends with the manufacturing of cotton curtains, finally to different disposals.

The manufacturing process of cotton contains all the sub-processes, spinning, weaving, dyeing, and finishing. The applied FR is the durable organophosphorus and nitrogen-containing monomeric or reactive species, which stands more than 50 launderings (Horrocks and Price, 2001). However, at the end-of-life of FR cotton fabric, we applied AOP treatment to degrade and remove the FR substance from the fabric and leads to general disposals, such as incineration, landfills and gasification. The analyzed end-of-life scenarios were:

3.7.3.1 End-of-life landfill scenario 1 (S1)

It's the reference case for the FR cotton fabric with landfill as a disposal, where the textile product follows all the manufacturing, distribution, use and end-of-life phases and ends to landfill directly. The FR treatment is considered as a part of the finishing process. In literature, finishing process found to requires as much as 1 kg chemicals and auxiliaries for 1 kg of finished textile (Muthu, 2014). However, it is assumed a FR curtain contains 250-300 gm of FR substance or species on it, which goes till its disposal. The wearing off or abrasion and volatilization of FR was not considered.

3.7.3.2 End-of-life landfill scenario 2 (S2)

In the second landfill scenario, proposed eco-design is applied which is the AOP treatment to the FR cotton fabric at the disposal stage and then landfilled. A strong oxidation reaction from AOP will degrade and remove the FR substance from the fabrics. The potential environmental impacts of landfill scenario 2 (S2) were evaluated and compared with the reference landfill scenario 1 (S1).

The calculation of landfill scenario after eco-design applied to the FR curtain is estimated on the fact that the FR species or substance have been degraded and removed from the fabric. An assumption of FR species was taken which goes with the FR cotton curtain to the disposal. Similarly, no wearing off or abrasion and volatilization of FR was considered. Moreover, for simplification and general perception of end-of-life phase, any additional particulates are not

considered, since the fabric goes through Fenton's reaction and alters the thermogravimetric properties of the fabric.

3.7.3.3 End-of-life incineration scenario 1 (S1)

This scenario focused on replacing landfill with incineration process at the disposals of FR textiles. Incineration scenario 1 was considered as a reference case for the LCA of FR textiles with incineration at the end-of-life phase. Moreover, incineration scenario 1 (S1) has all the same phases manufacturing, distribution, and use phase. In incineration, the FR cotton curtain is burned and the energy recovered is assumed to be utilized for heat/steam generation for electricity.

3.7.3.4 End-of-life incineration scenario 2 (S2)

The fourth scenario is about the incineration of the FR cotton curtains which undergoes through proposed eco-design at its disposal. The calculation of incineration scenario after eco-design applied to the FR curtain is estimated from the calorific increase mentioned under heat release results, which states an increase of 51% in total heat release (THR) [kJ/g] values during combustion after the degradation of FR species or substance from the fabric. Thus, the amount of heat energy recovered while the incineration of FR cotton curtain after eco-design applied was incorporated into the LCA software (EIME) accordingly.

3.7.3.5 End-of-life gasification scenario 1 (S1)

It's the reference case for the FR cotton fabric with gasification with end-of-life as disposal. Similarly, the textile product follows all the phases and ends at the gasifier directly. The calculation of gasification scenario is carried out by evaluating the possibility of gasification of FR textiles (whether FR textiles can be gasified or not), increase or decrease in gasification temperature (energetic yield) and qualitative and quantitative analysis of produced gas when the FR textile product is gasified.

3.7.3.6 End-of-life gasification scenario 2 (S2)

This scenario is modeled on the outcomes of the all three parameters discussed in gasification reference case scenario, which is gasification possibility, energetic yield, and syngas from the gasification of FR cotton textile after the degradation and removal of the FR species with the help of AOP. As aforementioned, an incomplete combustion of textile products with FR species leads to toxic emissions (Simonson, 2000) and theoretically, FR resists the combustion, similarly, it may alter the syngas composition. The degradation and removal of the FR species from the cotton textile will certainly give different composition syngas and energetic yield than the one with FR species. The estimations of the gasification scenario 2 (S2) was based on the qualitative and quantitative analysis of above mentioned parameters during the gasification.

Table 6. Built LCA end-of-life scenarios for the FR cotton curtain

Disposals	End-of-life scenarios	Description
Landfill	Scenario 1 (S1)	Without Eco-design
	scenario 2 (S2)	Eco-design applied
Incineration	scenario 1 (S1)	Without Eco-design
	scenario 2 (S2)	Eco-design applied
Gasification	scenario 1 (S1)	Without Eco-design
	scenario 2 (S2)	Eco-design applied

3.7.4 Life cycle impact assessment

The LCA results differ significantly depending on used data sources, assumptions and especially system boundaries. Accordingly, this LCA of FR cotton fabric starts from the raw cotton and spinning, which includes all the processes for instance, opening, cleaning, carding, drawing, roving etc., weaving, wet processing, FR treatment, curtain manufacturing, distribution, usage (washing, drying, ironing) and finally ends at the disposals.

Despite the fact that the FRs are applied to textile products to bring safety to the surroundings or the wearer from the accidental fires, these are possibly needed to burn to perform their function. In addition, in fire incidents, the burning of different type of FRs can produce extremely toxic substances and are released into the atmosphere. However, the focus of this

study is in the end-of-life phase of FRs after being disposed of, so the environmental impacts of the FR curtains are considered as most relevantly without any fire incidents. Moreover, energy recovery was considered in valorization cases for comparative environmental impact analysis.

3.7.4.1 *Studied environmental impact categories*

The latent environmental impacts considered for this work were expressed at mid-point level. The assessed impact categories were: Air Acidification (AA) [AE], Global Warming Potential (GWP) [kg CO₂ eq.], Air Toxicity (AT) [m³], Freshwater Ecotoxicity (FWE) [CTUe], Ozone Depletion Potential (ODP) [kg CFC-11 eq.], Photochemical Ozone Creation Potential (POCP) [kg NMVOC eq.], Terrestrial Ecotoxicity (TE) [kg 1,4 - DB eq.], Raw Material Depletion (RMD) [person reserve], Water Eutrophication (WE) [kg PO₄³⁻ eq.] and Water Depletion (WD) [dm³].

Chapter 4

Degradation and Elimination

4.1 Degradation of flame retardants

The aforementioned none/semi-durable FRs, such as DAP and APP (in section 2.2 Types and applications of FRs) and their associated toxicity, seems futile to be degraded with Fenton's reactions. Since, the FR DAP is highly water soluble and removes easily from the fabric with simple water wash. However, the washed away FR can degrade water or soil at disposal. To cope with the degradation of none durable FR, infra-red (IR) radiation was used to degrade the FR from the cotton textiles prior to its disposal (Conference Paper III). The IR degradation of none/semi durable FR from textiles were found to be successful. However, the IR degradation technique was found insignificant for the durable FRs; therefore in this thesis, focus was given on the degradation of durable FR with Fenton's reaction.

4.1.1 Degradation of FR in aqueous form

Figure 11 shows the COD reduction with respect to time with a decrease of around 2000 mg/l in COD value in the early 30 minutes, confirming the ability of Fenton's reagents to degrade the FR species and other additives. FR treated cotton fabrics were thus prepared for in-situ degradation with Fenton's reagents. Moreover, for in-situ degradation of FR from textiles, COD reduction approach was employed for the first time with the physical presence of cotton fabric, which may lead to irregular results; therefore assumed values were taken where needed and general standards were evaded.

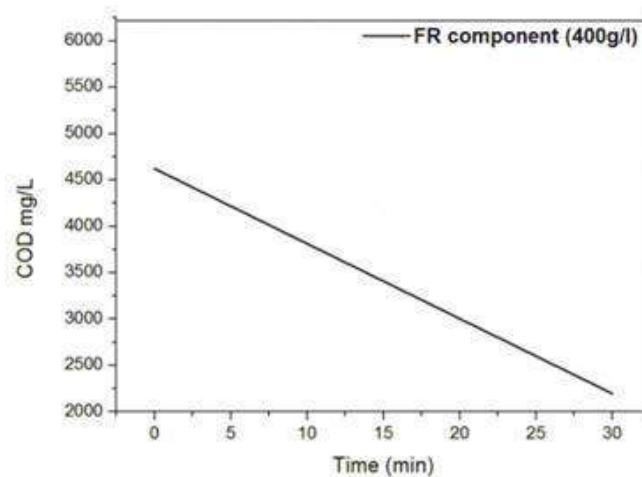


Figure 11. COD reduction with time of FR aqueous solution of free MDPA (400g/l) in with Fenton's reagents $\text{FeSO}_4/\text{H}_2\text{O}_2$ (2/6g/l) (Paper I)

4.1.2 *In situ degradation of flame retardant on cotton fabric*

The amount of 400 mg of FR products was deposited on each fabric sample (32 x 18 cm) using the padding process with the 400 g/l FR aqueous solutions. Thus, lower concentrations of Fenton's reagents were tested for the in-situ degradation of the FR on FR treated cotton fabric. Indeed 3 different concentrations of the ferrous source were used: 100, 200 and 500, mg/l, while the quantity of hydrogen peroxide catalyst was kept constant at 1 g/. It has been observed that the Fenton's reaction becomes vigorous at higher H₂O₂ and Fe²⁺ quantities, as it raises the temperature of reaction solution more quickly and also affects the hydroxyl radical (OH•) consumption. Degradation of MDPA FR from the cellulosic fabric was monitored by flame test and change in thermogravimetric curves.

4.2 Characterization results of degradation

4.2.1 *Flame test*

A flame test was carried out according to the French standard NF-G 07-113; 1972 to evaluate the flammability of FR treated cellulosic fabrics before and after Fenton's reaction. According to this fire resistance testing, samples were classified by measuring the burnt surface area of the fabric sample and the duration of the afterglow which is considered as an important parameter. Here the afterglow was not taken into consideration as the duration was less than standard time. The afterglow is considered significant if the heat source went off and the sample shows afterglow since it shows the burning aptitude of the fabric without the initial flame.

Table 7. Flame test on the cotton fabric samples after FR treatment and Fenton's reaction

Samples	Weight before test (gm)	Weight after test (gm)	Classes according to NF-G 07-113
Control	6.10	2.42	E
MDPA treated	6.15	5.65	A
After Fenton's reaction (100mg/l: 1g/l)	6.08	5.12	C
After Fenton's reaction (200mg/l: 1g/l)	6.10	4.90	C
After Fenton's reaction	6.09	3.52	D

(500mg/l: 1g/l)

(100mg/l: 1g/l, 200mg/l: 1g/ and 500mg/l: 1g/l) are the used reagent fractions of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$: H_2O_2

The flame spreads slower on MDPA treated fabrics after the fire ignited, keeping the afterglow for a short time only and the sample was positioned in class A, which is the best class for this test standard (see Table 7). A marginal, but longer afterglow was observed for samples which were subjected to Fenton's degradation as compared to untreated (control) and MDPA treated samples. In the case of the control cotton samples, there was no fabric left, but only ashes were left on the sample holder.

4.2.2 COD reduction

The reduction of COD in Fenton's reaction solution can be seen in the Figure 12. The initial COD of the solution was considered (422 mg/l) as it was the COD value of FR on the cotton fabric samples. The Fenton's reagent with higher concentrations showed more than partial degradation of FR in one-hour reaction.

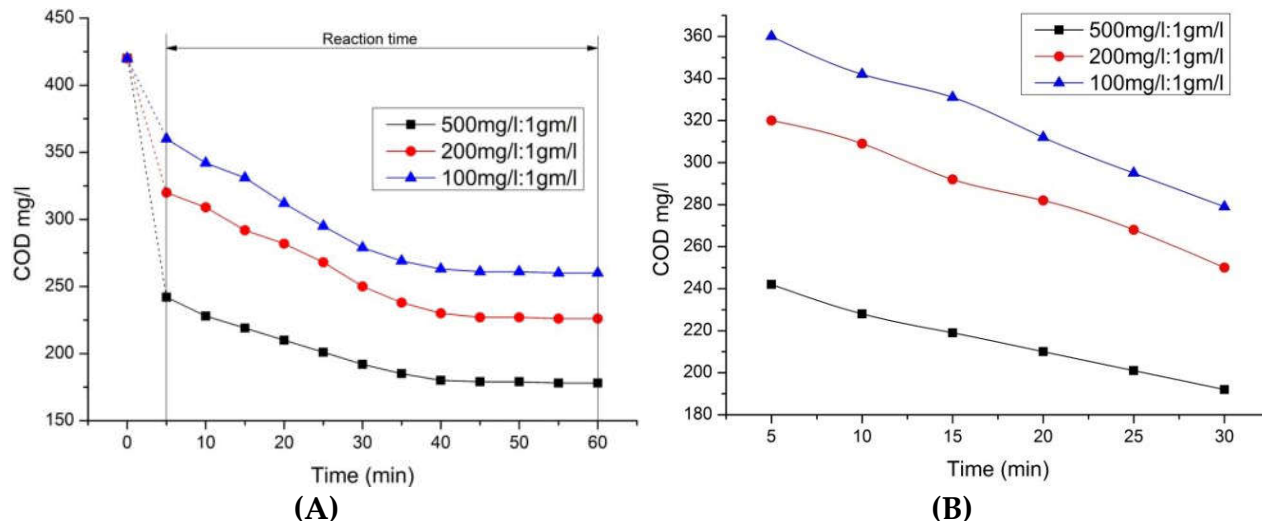


Figure 12. COD reduction with Fenton's reagents from FR treated cotton fabric in the reaction solution, (A) COD values in an hour of Fenton's reactions (B) COD values in the first 30 minutes of Fenton's reactions (Conference Paper I)

Different concentrations of $(\text{H}_2\text{O}_2/\text{Fe}^{2+})$ can be suggested when it comes to COD reduction by Fenton's reaction, as the optimum ratio depends upon the organic compounds selected for the

degradation. In this experiment, the concentration of H_2O_2 was kept constant and Fe^{2+} was varied, as higher concentrations of H_2O_2 may affect the hydroxyl radicals' ($\text{OH}\bullet$) consumption in the degradation process. The COD reduction of the reaction solution increases regularly in the beginning 30 minutes then slows down. The COD removal of the experimental solution increases with increasing the Fe^{2+} concentration, as a less number of $\text{OH}\bullet$ are generated by the oxidation of MDPA at lower concentrations.

From the Figure 12, it can be seen that the higher concentrations of Fenton's reagent showed rapid and higher mineralization of MDPA FR species. Therefore, highest concentrations used for the FR degradation with Fenton's reagents (500mg/l of $\text{FeSO}_4\cdot 7\text{H}_2\text{O}$ and 1g/l of H_2O_2), was considered for further characterization results.

4.2.3 Thermogravimetric analysis

The thermal decomposition of cotton fabric includes different stages. The first stage concerns the release of adsorbed water, which starts around 100 °C. During the second stage, there is a fast weight loss due to decarboxylation and dehydration reactions producing combustible gasses such as ketones, aldehydes, ethers, etc. The third stage starts around 500 °C and corresponds to the decomposition of char formed during the second stage (Xing et al., 2011).

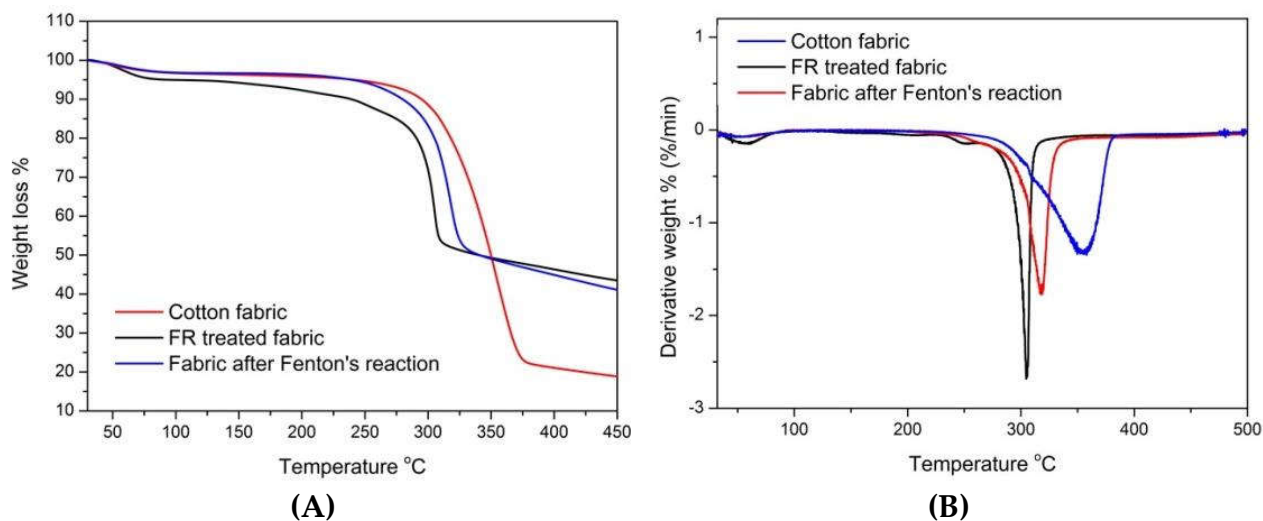


Figure 13. TGA (A) and dTGA (B) curves of the cotton fabric and FR treated fabrics before and after Fenton's reaction (concentration 500mg/l: 1gm/l) (Paper I)

The TGA curves in Figure 13A show the similar three-stage combustion behavior of the cotton fabric. Below 300 °C, there is a little weight loss due to moisture loss, the decomposition of the cellulose and a fast weight loss occurs amid 300-370 °C. Decomposition of char occurs above 370 °C, results in a total residue of 16.1 % (Table 8). However, the weight of the FR treated fabrics initially decreases quickly utmost at decomposition temperatures, which enable them to produce more residues (43.5 %) than the untreated cotton fabrics. The FR treated fabric loses moisture below 300 °C, the onset temperature occurs at 290.5 °C, above this is the main degradation temperature of the FR treated cotton fabric. The decomposition of char forms above 300 °C for the FR treated fabric. The MDPA FR finishes work as a condensed-phase retardant and help char formation (Egyed and Simon, 1979). The phosphorus and nitrogen synergism increase the char formation, and the MDPA produces the greatest char at higher temperatures generating high levels of aromatic volatiles such as toluenes, benzenes, and phenols (Horrocks, 1996).

The characteristic degradation temperatures, such as onset temperature, which denotes the temperature at which the weight loss begins, the degradation temperature at the maximum mass loss rate (T_{max}), and the residue percentage is presented in Table 8. Although, the FR treated cotton fabrics with highest concentrations of Fenton's reagents used, showed a similar curve trend as compared to FR treated cotton fabric, but it's changing the curve trend towards cotton fabric. The FR cotton fabric after Fenton's reaction starts to decompose later than the FR cotton fabrics. The char formation around 320 °C has also been reduced as compared to the FR treated cotton fabric, suggesting a visible change in thermogravimetric properties of the fabric after Fenton's reaction. The FR treated samples with higher concentrations of Fenton's reagents also showed visible curve changes from DTG (Paper I).

Figure 13B shows that the derivative thermogravimetric curves have only one peak in all the samples, which indicates that the maximum weight loss of all the sample fabric samples occurs at a certain thermal decomposition stage. The weight loss of FR treated fabric after Fenton's reagents is reduced, as well as the total residue is decreased at the end of the thermogravimetric analysis (see Table 8).

Table 8. TGA data of FR treated cotton fabric and after Fenton's reaction (Paper I)

Fabric samples	Onset temp	Degradation temp	Residue (%)
	(°C)	T _{max} (°C)	
Cotton	317.2	370.1	16.1
FR treated	290.5	304.5	43.5
After Fenton's reaction	304.2	334.5	32.2

4.2.4 Pyrolysis combustion flow calorimeter (PCFC)

The PCFC parameters of the cotton fabric are shown in Table 10. The HRR curves of the cotton fabric treated with MDPA and after Fenton's reaction (concentration 500mg/l: 1gm/l) are presented in Figure 14. The data presented in Table 9 show that the HRC and PHRR decrease from 260 J [g.k] and 248 w/g to 80 J [g.k] and 58 w/g in the comparison of MDPA treated the cotton fabric with untreated cotton fabric. The increase in char yield indicates the decomposition of the FR on the fabric. The decomposition of MDPA FR on the fabric at a lower temperature is determined as its effectiveness.

Table 9. PCFC parameters of the FR cotton fabric after Fenton's reaction (Paper I)

Cotton samples	HRC (J[g.k])	Peak HRR (w/g)	Total heat release (kJ/g)	T _{PHRR} (°C)	Char yield (%)
Cotton fabric	260	248	10.1	360	5.9
FR treated fabric	80.0	58	3.5	280	31.8
After Fenton's reaction	160	146	6.8	300	18.0

The HRR curves presented in Figure 14 shows a decrease in HRR as the cotton fabric is compared to MDPA treated FR cotton fabric. Meanwhile, FR treated cotton fabric after Fenton's reaction shows a visible increase in HRC and PHRR from 80 J [g.k] and 58 w/g to 160 J [g.k] and 146 w/g. The char yield also decreases when the FR cotton fabric goes through the Fenton's reaction, which yields to the higher heat release rates. The HRR values increase in the case of FR cotton fabric after Fenton's reaction presenting a decrease in the decomposition of MDPA on the fabric. This indicates a condensed phase mechanism of the FR, as it decreases the quantity of fuel produced during the thermal decomposition (Paper I).

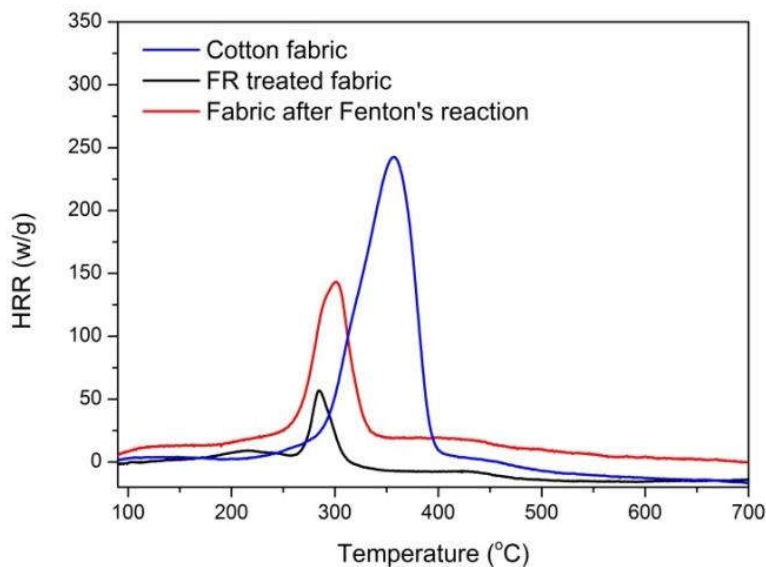


Figure 14. Heat release curves of cotton fabric and MDPA treated fabrics before and after Fenton's reaction (Paper I)

4.2.5 Mechanical properties

To assess the mechanical properties of cotton fabrics before and after Fenton's degradation, the tensile strength of the fabrics was measured in both warp and weft directions before and after Fenton's reaction (concentration 500 mg/l: 1 gm/l).

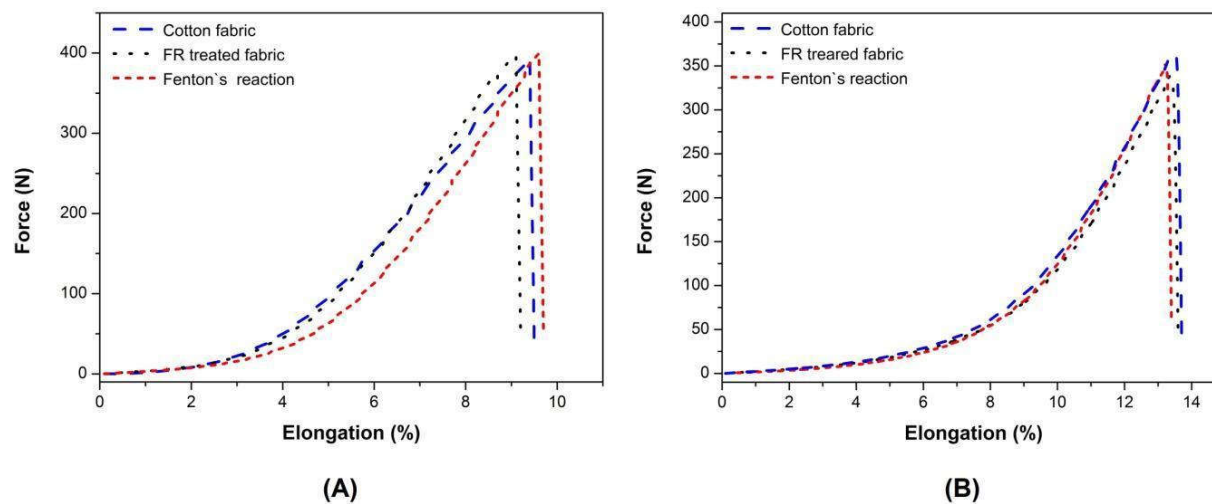


Figure 15. Tensile properties of cotton fabrics after Fenton's reaction (A) cotton fabrics along the weft direction (B) cotton fabrics along the warp direction (Paper I)

Mechanical attribution of fabrics is mandatory if it is considered for re-usability as an alternative valorization. Figure 15, shows the tensile strength values plotted against elongation in the weft (A) and warp (B) directions. The results show that the tenacity and the elongation at break of the FR cotton fabrics are similar to that of the untreated cotton fabric, and the FR cotton fabrics subjected to Fenton's degradation did not lose their tensile properties.

4.3 General discussion

The "*in-situ* degradation" of durable FR cotton fabrics can be effectively carried using Fenton's reagents ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O} + \text{H}_2\text{O}_2$) which allow advanced oxidation reactions. Our studies show that the concentration of Fenton's reagents used has an influence on the rate of degradation which is measured by thermal analysis of the cotton fabrics after Fenton's reaction. Higher concentrations of ferrous salt lead to higher rate of degradation. A partial degradation of MDPA from the aqueous media was observed to be occurring in 30 minutes with given Fenton's reagents used.

The mechanical properties of the cellulosic fabric after the advanced oxidation reaction from Fenton were unaltered in both warp and weft directions. The concentrations used are appropriate for FR degradation while the cotton fabrics retain their tensile strength. Indeed, past studies report the powerful abilities of Fenton's reagent to decompose cotton fibers: 5 mg of cotton was decomposed completely in 7 days using 0.2 mM ferrous source (FeSO_4) and 0.4% hydrogen peroxide (H_2O_2) at pH 4.2±4.3 (Rättö et al., 1997). On the other hand, Fenton's reaction used on cotton linters for a period of 48 hours, with 0.5 mM ferrous source (Fe^{2+}) and 2.0% hydrogen peroxide (H_2O_2) optimized surface pre-treatment of cotton fibers (Jain and Vigneshwaran, 2012).

Flame test of the FR cotton fabrics confirms a decrease in flame resistance and confirmed the degradation of MDPA FR from the fabric. The FR degradation was also confirmed by the TGA experiments. Our studies using Pyrolysis combustion flow calorimeter confirm that there is a higher heat release after Fenton degradation of the FR from the FR fabrics. The increase in heat release rate of degraded FR cotton is interesting for energy production by incineration as

compared to FR cotton fabrics. Based upon the thermogravimetric behavior aforementioned, it is believed that the extremely high oxidation $\text{OH}\cdot$ radicals from Fenton's reaction are responsible for the decrease in the residue and the increase in degradation temperature of the FR cotton fabric. By considering the results obtained from this work, we propose a general reaction mechanism for degradation and mineralization of MDPA bonded to cellulose via TMM by oxidative action of hydroxyl radicals in the Fenton's reaction process, shown in Figure 16.

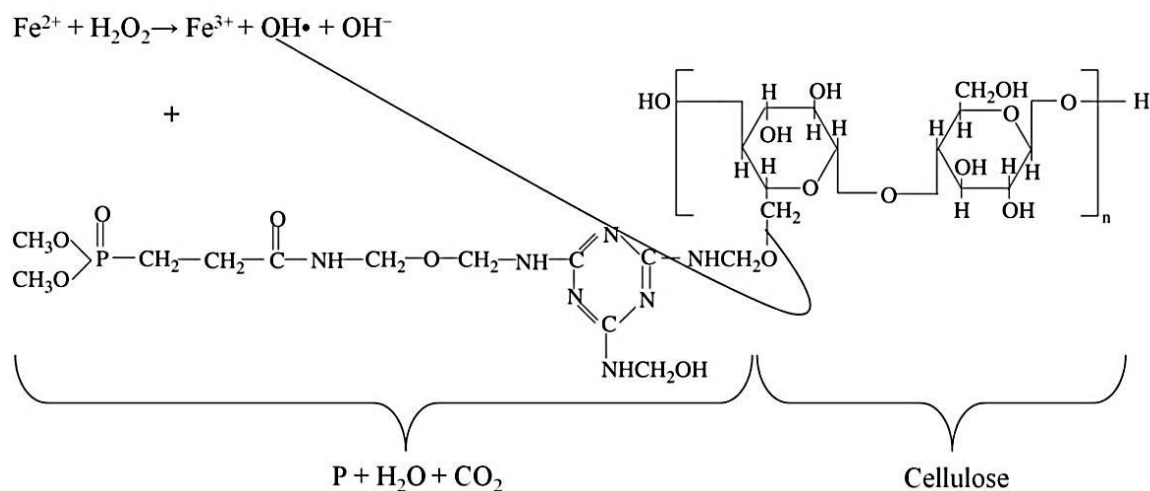


Figure 16. Proposed reaction pathway for the mineralization of MDPA bonded on cellulosic fabric by Fenton process (Paper I)

The degradation of MDPA seems to occur in a similar mechanism as other organic compounds, as some authors have indicated in their work. Due to the complexity of the Fenton's reactions, Kang et al. (Kang et al., 2002) have classified the reactions in possible three categories: inorganic reactions involving H_2O_2 and Fe^{2+} , Fe-organic reactions that influence the Fe-redox cycle and inorganic-organic reactions leading to mineralization.

The degradation of organic compounds by the $\text{OH}\cdot$ radicals can be described by several reaction mechanisms. The $\text{OH}\cdot$ radicals can react with the organic compounds by abstracting H from N-H, O-H or C-H bonds, by adding to conjugated aromatic rings or adding C-C bonds. It is postulated that the remote MDPA components from the fabric and a reaction solution are further mineralized into water, carbon dioxide, and other particulates. The degradation of FR

assumably occurs in a similar way as other organic compounds do. Due to the complications of Fenton's reactions, (Kang et al., 2002) has categorized the reactions in three possible groups: inorganic reactions involving H_2O_2 and Fe^{2+} , Fe-organic reactions that influence the Fe-redox cycle and inorganic-organic reactions leading to mineralization. Moreover, the degradation of organic compounds by the $\text{OH}\cdot$ radicals can be described by several reaction mechanisms. The $\text{OH}\cdot$ radicals can react with the organic compounds by abstracting H from N-H, O-H or C-H bonds, by adding to conjugate aromatic rings or adding C-C bonds (Kang et al., 2002). Degradation kinetics of Fenton's reaction produces multipart and large results in complex rate constants which vary studies to studies. Some studies related to Fenton's process kinetics can be found in the literature states same complexity rate constants (Ramirez et al., 2009). Details on the degradation and its kinetics of MDPA FR from cotton fabrics can be found in (Conference Paper I).

As the aim of this study was to degrade the FR from the cotton fabric's surface without damaging the cotton fabric, it was crucial to reduce the Fenton's reaction time period of one hour. This study shows that this time interval can allow degrading significantly the durable and permanent FR product from the cotton fabric. However, the degradation of the FR can be enhanced by using various reaction combinations, for instance, Fenton's reactions with different pH solution and reaction temperatures, Fenton-like reactions, and UV-Fenton etc.

Chapter 5

Thermal Valorization by Gasification

5.1 Thermal valorization of textile pellets

5.1.1 Gasification of textile pellets

Gasification is considered as a beneficial method to convert organic materials or biomass into a multipurpose gas known as syngas (synthesis gas). In recent years, the energy valorization of non-conventional resources to save fossil fuels and reduce the generation of domestic and industrial waste has gained a great attention.

Accordingly, the waste is transformed into a valuable energy source instead of being disposed of. To have a better understanding of the gasification process, a customized spouted bed having an unusual geometry (square based instead of circular one) was developed for an easier scale-up. The spouted bed gasifiers can perform better in hydrodynamic control, due to a low gas flow rate and pressure drop lower than conventional bubbling fluidization. In order to understand the behavior, hydrodynamic control of prepared textile pellets density was examined by feeding it to a granular bed made of a stationary inert phase, which acts as a thermal and hydrodynamic buffer.

5.2 Characterization results of gasification

5.2.1 Thermal transitory analysis

The rationale of preliminary experimentation is given by the order of different LPG/air ratios to establish a feasibility of easy reaction control over all possible operations (combustion, pyrolysis or gasification). Normally, the initial step involves the pre-heating of spouted bed to about 400 °C (by reading the thermocouple output in the sand bed); this temperature assures the ignition point of prepared textile pellets having a standard composition. This step was carried out by regulating the furnace thermal power at 11 kW with a suitable LPG flow rate and minimal extra-stoichiometric air.

The desired temperature was reached in about 60 min, as shown in Figure 17A. A solid particulate combustion mode in the spouted bed was then chosen to speed up the whole reactor heating and reach the actual gasification temperature. The prompt peak of temperature at 90

min was given by the oxidative region. Subsequently, the air flow was decreased to have a reducing reaction mode (endothermic pyrolysis) in the 90 to 110-minute intervals. There is a partially oxidative region to gasify the pyrolytic solid residue previously generated followed by regulating the LPG flow and water spraying in the pre-burner to maintain an adequate in-line steam generation.

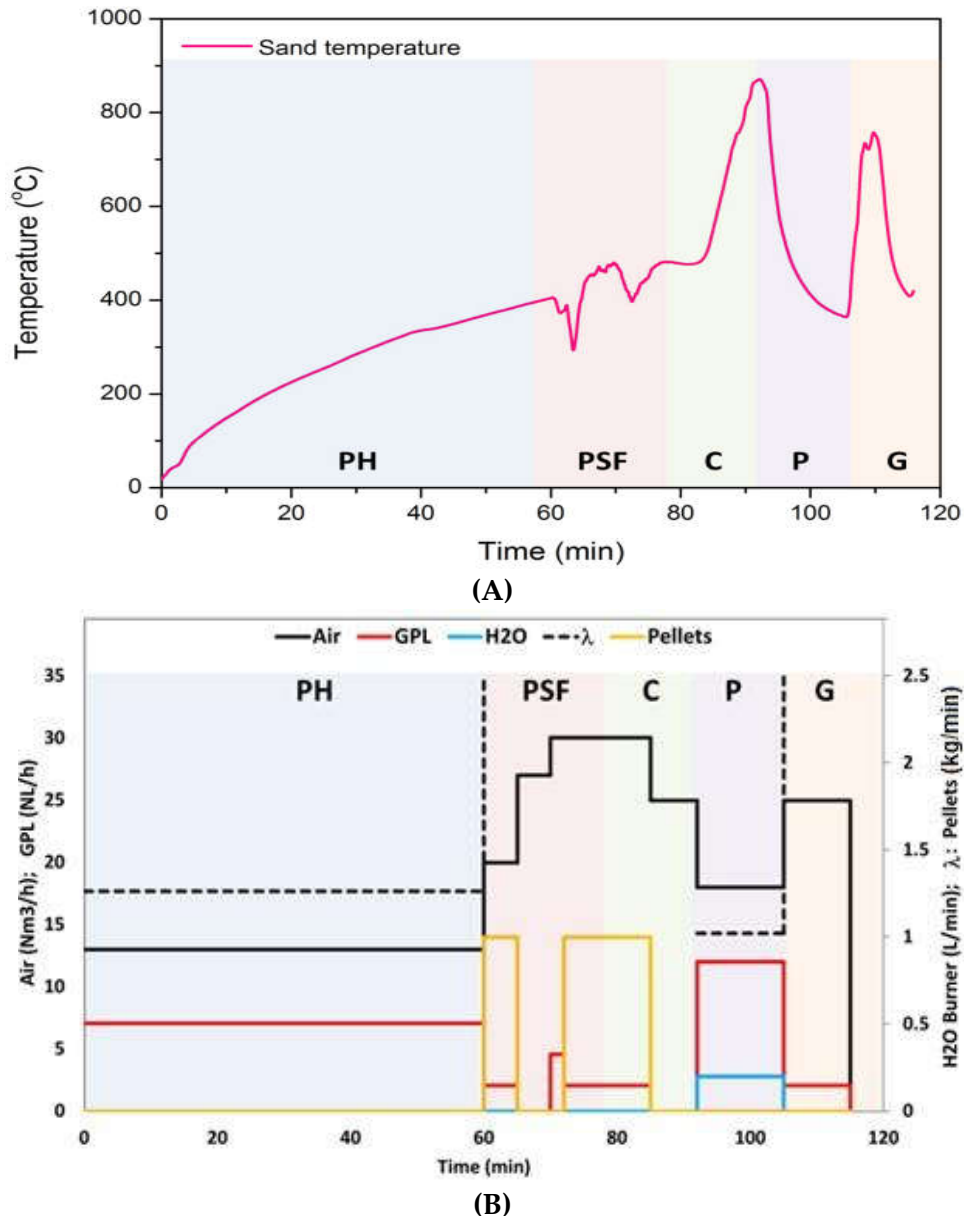


Figure 17. Thermal transitory (A) Flow regulation (B) in the spouted bed gasifier with pre-heating (PH), pulsating solid feeding (PSF), combustion (C), pyrolysis (P) and gasification (G) regions (Paper IV)

Figure 17B shows the different flow rates and thermal transitory in variant conditions tested. The pre-heating of the bed initiated at about 400 °C in 60 min at 11 kW. At this pre-heating stage, a few amounts of wood pellets were added into the reactor, which helps in a reduction in LPG flow rate and the increase of the air flow rate. This leads to the high oxidizing atmosphere ($\lambda \approx 1.20$, which is the stoichiometry ratio between oxygen and gaseous fuel) for a total combustion of the feed material, providing an additional energy boost and enthalpy of the reaction transferred to the rig causing a sudden temperature increment.

Higher temperatures lead to higher conversion efficiency, thus affect the produced gas contents (hydrogen, carbon dioxide, carbon monoxide and methane) and consequently increase the yield. The temperatures beyond 750–800 °C, leads to steam forming and water-gas reactions due to the endothermic nature of the H₂ production reactions, which consequently increase the hydrogen content and decrease the methane content. Temperatures above 850–900 °C results in increase of carbon monoxide and decrease in tar contents due to high steam reforming and destruction of tar (Kumar et al., 2009). This increment of temperatures increases the gas yield.

5.2.2 *Gasification temperature*

It is important to maintain a high temperature in order to attain the gasification process. A radial temperature distribution was checked using the thermocouples as mentioned in section 3.5.4 (Temperature control at the rig). In gasification plant, the temperature must expand progressively in order to expel the excess water moisture present in the solid matrix. This operation requires a few hours and ought to be revised for various cycles. Generally, the plant heated up from room temperature to reach suitable gasification temperature by feeding cheap solid fuel: it was done with wood pellets to avoid wastage of prepared textile pellets. The burner was set at 11 kW thermal power, with a marginal of air flow ($\lambda = 1.2$).

From Figure 18, it can be seen that the gasification of both the masses, FR cotton pellets (before and after degradation) are in a regime of low-temperature gasification. Whereas, the low-temperature gasification occurs at ($\sim < 1000$ °C), while the high-temperature gasification ($\sim >$

1200 °C). In low-temperature gasification (or lean gasification to produce low BTU gas), air is used as a gasifying medium, which leads to undesired nitrogen into the gas (Basu, 2013).

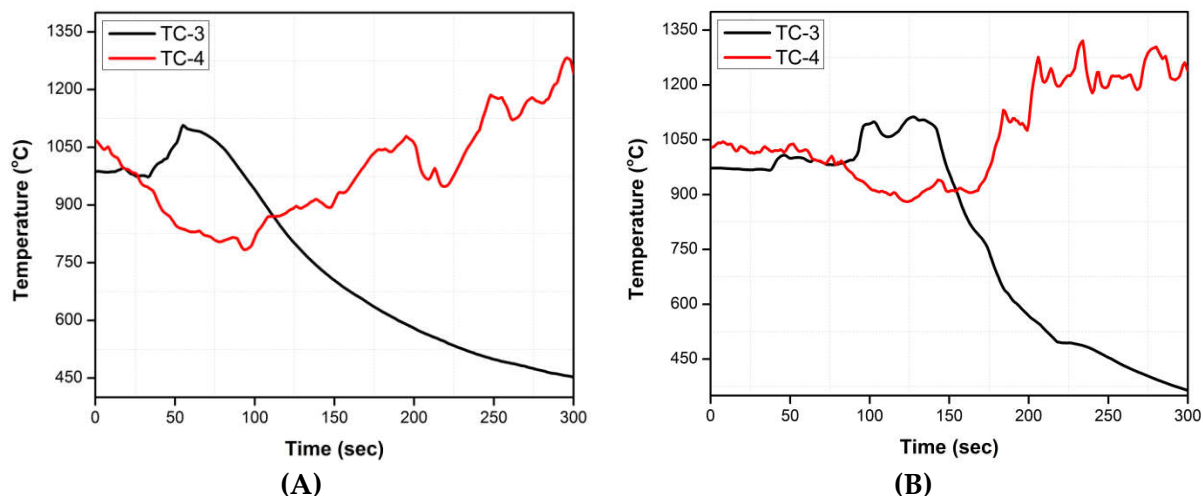


Figure 18. Temperature variation among TC-3 (sand) and TC-4 (fountain) of FR textile pellets (A) and FR textiles after degradation (B)

5.2.3 Analysis of gas evolution

5.2.3.1 Flame retardant cotton and gas evolution

The gas components produced by the gasification of the textile feed (FR cotton and cotton after degradation of FR) were in-line sampled from the off-gas piping line. The lag transport time between continuous sampling and gas analysis was close to 60 seconds. The gas components were analyzed: CO, CO₂, H₂ and CH₄ concentrations were given the maximum emphasis. The composition of gas was converted into a mass flow rate by calculating the measured composition and total gas flow rate. It is essential to consider the evolution of other components during the gasification process, for instance, the heavier hydrocarbons along with carbon monoxide (CO) and hydrogen (H₂) (Basu, 2013). These heavier hydrocarbons are further broken into other components and can be used for other applications. Figure 19 shows the volatile gas components, such as CH₄, ethane, acetylene and ethylene. Figure 20 shows the composition of the gas evolved from the gasification of FR cotton pellets.

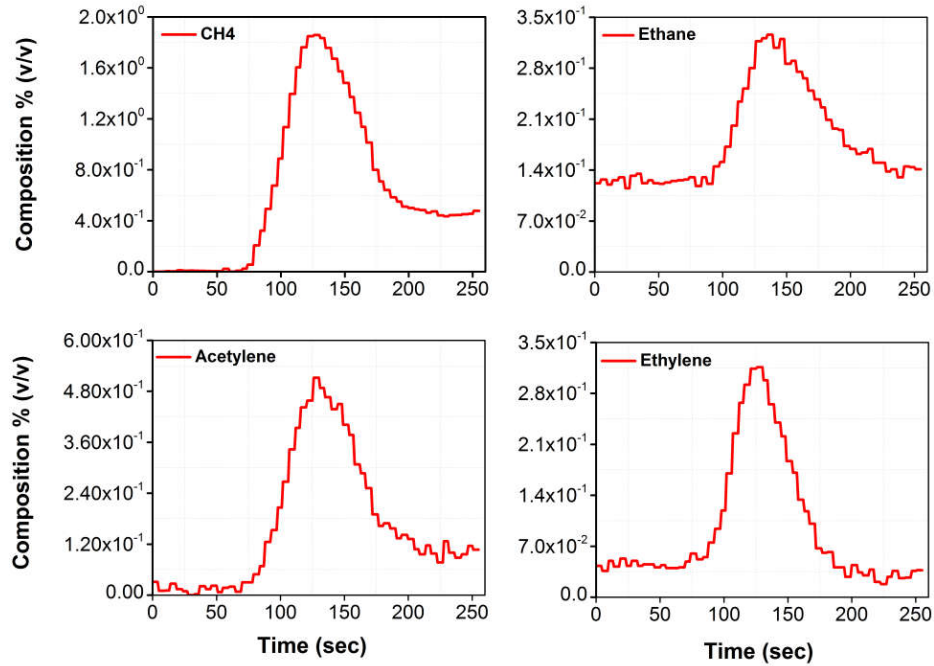


Figure 19. The composition of gas evolved during the gasification of FR cotton pellets. For the volatile components of CH₄, ethane, acetylene and ethylene

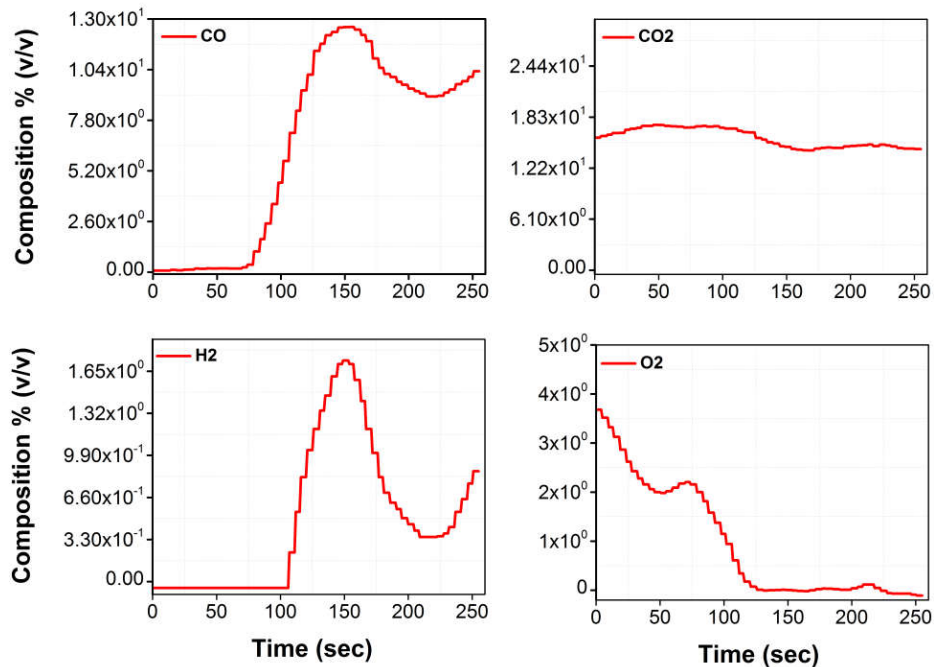


Figure 20. The composition of gas evolved during the gasification of FR cotton pellets. For the volatile components of CO, CO₂, H₂ and O₂

5.2.3.2 Flame retardant cotton after degradation and gas evolution

There can be many components present in the evolved gas from the gasification process and are linked to various factors, which can affect the outcomes of the evolved gas. For instance, during the elevation of the pyrolysis temperatures, components like H₂O, CO₂, CH₄ and other low-molecular-weight gasses continue to increase.

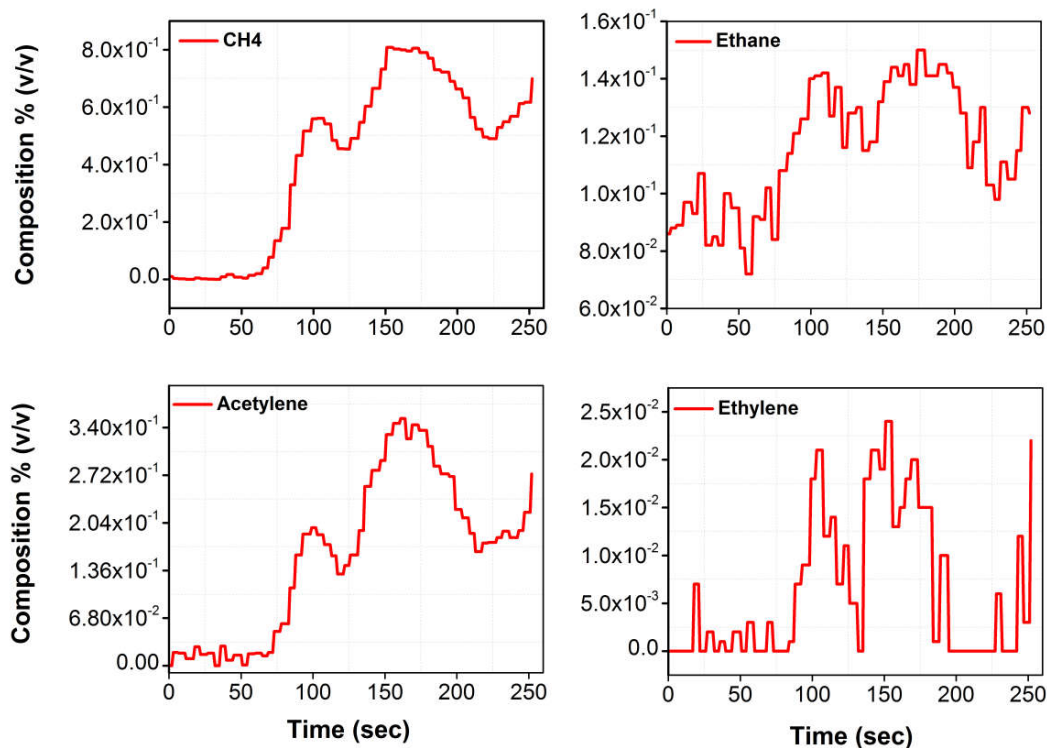


Figure 21. The composition of gas evolved during the gasification of FR cotton pellets after the degradation with Fenton's reaction. For the volatile components of CH₄, ethane, acetylene and ethylene

In combustion, the cotton fabric being treated with FR containing phosphorus and nitrogen elements probably starts with the catalyze reactions of dewatering, decarboxylation, and charring (Wu and Yang, 2007). Similarly, the FR species on the cotton fabric resists in a complete combustion of cotton. Moreover, the hurdle in gasification of FR cotton fabric would be an evolution fragmented products in gas. As aforementioned, for a good gas composition, with a minimum quantity of impurities and more energy conversion efficiency, the optimized

gasification parameters and conditions are required. For the gasification of a particular shape and sized pellets of FR cotton, flow rate [150 g/min] was found optimal. To avoid the overfeeding of mass and plugging, the flow rate was starved, which led to irregular gas yield.

From Figure 21 and 22, a non-constant gas yield was monitored; this was due to a problematic feeding of low-density fibrous material into the small-scale gasification pilot unit designed for this project. This serious scale-down drawback is expected to be overcome by the planned process scale-up. Due to this difficulty, the gas yield with averaged composition values was calculated and is mentioned in the following section. Hence, as a final consideration, it is important to have a constant flow rate of solids for the maximum energy efficiency of the gasification system.

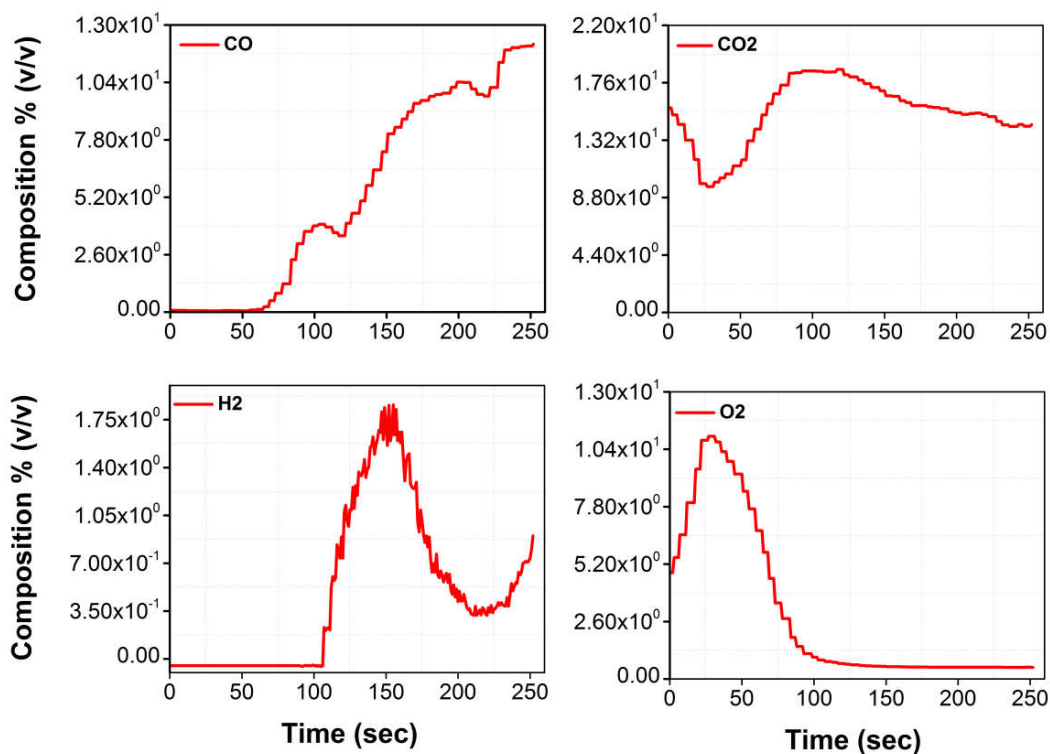


Figure 22. The composition of gas evolved during the gasification of FR cotton pellets after the degradation with Fenton's reaction. For the volatile components of CO, CO₂, H₂ and O₂

5.3 General discussion

The utilization of FR is increasing each year with a prime role in textile products is mainly expected to suppress rapid combustion. Apart from the positive effect of FR, these have generally some negative effects. For instance, FR applied to textile products may inhibit an incomplete combustion of textiles, and it deteriorates thermal recovery efficiency of textile products. However, degradation of FR substance from textiles would increase the combustion properties of the FR textile products.

From the Table 10, a very moderate difference in gas compositions was observed between the FR cotton and FR cotton after degradation of FR species with Fenton's reaction. However, the average temperature is higher for the FR cotton after degradation of FR species, since the removal of FR species improves the combustion/gasification. The cotton textiles treated with FRs, for instance, organophosphorus species have lower decomposition temperatures due to catalyzed dehydrations of cellulose by the phosphorus acid (Vukušić et al., 2011). This phenomenon leads to incomplete combustion of cotton textiles treated with organophosphorus species.

As mentioned earlier, the FR textile pellets were prepared manually, and wood pellets were fed initially to attain the gasification temperature, then finally prepared FR textile pellets were gasified. This irregular mass flow rate at the gasification caused irregular gas outcomes, averaged composition values are incomparable range. Energy valorization by gasification of FR textile products is achievable under controlled and standard conditions.

Table 10. Averaged composition values of the significantly evolved gas components during the gasification

Textile pellets	Mass flow rate (g/min)	Temperature (°C)		Gas composition % (v/v)				
		Annulus	Fountain	CH ₄	CO	CO ₂	O ₂	H ₂
Flame retardant	150	750	983	1.8	12.2	15.8	0*	1.8
Flame retardant after Fenton reaction	150	781	1064	0.8	12.1	15.33	0*	1.85

* Due to irregular syngas outputs, the oxygen (O₂) was evaded from the average composition. The values are calculated under the conditions of; bed inert material: silica sand (2 liters) and fluidization with air at 17 Nm³/h

From Table 10, the gasification temperature of FR cotton is lower as compared to the degraded FR cotton. The organophosphorus species of the FR used has nitrogen and phosphorus as active elements, which affect the pyrolysis reactions of cellulose in burning. For instance, the FR species decompose and generate phosphoric acid, which later polymerizes to polyphosphoric acids at relatively low temperatures.

These acids can catalyze the hydroxyl groups of cellulosic materials to dehydrate and carbonize and limit the pyrolysis reactions. Consequently, the production of water (H_2O), carbon dioxide (CO_2) and residue increases. On the other hand, the production of combustible products especially ketone, aldehyde, ester and ether are found to be reduced (Zhu et al., 2004). Moreover, FRs are also found to decrease the speed of pyrolysis of cellulosic materials (Zhu et al., 2004). The degradation of FR from the cellulosic material changes the pyrolytic properties of the material, which was found to be reduced due to the presence of FR species.

Since the feed mass for the gasification is cotton and the FR, the results primarily have a tendency to lower the decomposition temperature of the substrate. This lower decomposition temperature favors carbonization rather than depolymerization of the macromolecules, which results in higher char yield. Moreover, fewer volatile materials are present for gas phase combustion (Pandey et al., 2015).

Gasification is a thermo-chemical process which converts biomass through fractional oxidation into a mixture of syngas, consisting of CH_4 , H_2 , CO and CO_2 (Wang et al., 2008). Whereas, the oxidant can be air, steam, pure O_2 , and CO_2 or even their mixtures. The oxidant is one of the main parameters affecting the syngas composition. Due to abundant availability and zero cost, air is the most used gasifying agent. However, a large amount of nitrogen hinders the reaction parameters and affecting the syngas composition.

In addition, higher power blowers and bigger equipment are required. The nitrogen content issue can be overcome by using pure O_2 , which also gives better syngas but the operative cost is high. On the other hand, with a great abundant availability when there is no nitrogen issue and

with lower cost, steam is preferred having the advantage of increased heating value and H₂ content in produced syngas (Vecchione et al., 2013).

Chapter 6

Validation by Life Cycle Assessment

6.1 LCA of flame retardant textiles

After the degradation and elimination of the FR species, LCA was carried out to validate the proposed eco-design for the FR cotton textiles at their end-of-life phase. A detailed description of the LCA framework has been discussed in section 3.7 (Comprehensive LCA of FR textile). In this section, life cycle inventory analysis, scenario outcomes and overall LCA results of prominent impact categories are discussed. The scenarios which were studied are reminded in the Table below 11 (also in Table 6);

Table 11. Built LCA end-of-life scenarios for the FR cotton curtain (Reminder)

Disposals	End-of-life scenarios	Description
Landfill	Scenario 1 (S1)	Without Eco-design
	scenario 2 (S2)	Eco-design applied
Incineration	scenario 1 (S1)	Without Eco-design
	scenario 2 (S2)	Eco-design applied
Gasification	scenario 1 (S1)	Without Eco-design
	scenario 2 (S2)	Eco-design applied

6.1.1 Comparative inventory analysis

The primary data used in this study derives from the EIME software which includes databases such as, ELCD, Eco-Invent, and CODDE. All the processes in the textile manufacturing factory utilize steam for heating, and electricity for mechanical work, (spinning, weaving, wet processing, FR treatment, and textile manufacturing). Consumption of raw materials, electricity, and steam for these processes are estimated from pre-defined parameters in EIME software.

As can be seen in Figure 23, the utilized amount of renewable resources and emissions to air, water and soil in all the scenario cases are comparable, which leads to an obvious question that is whether there is a need to focus on end-of-life or not, moreover, what is the significance of applying the proposed eco-design. One understandable justification would be that all the cases follow same production, distribution, use phases as mentioned in the system boundaries (Figure 10, Chapter 3).

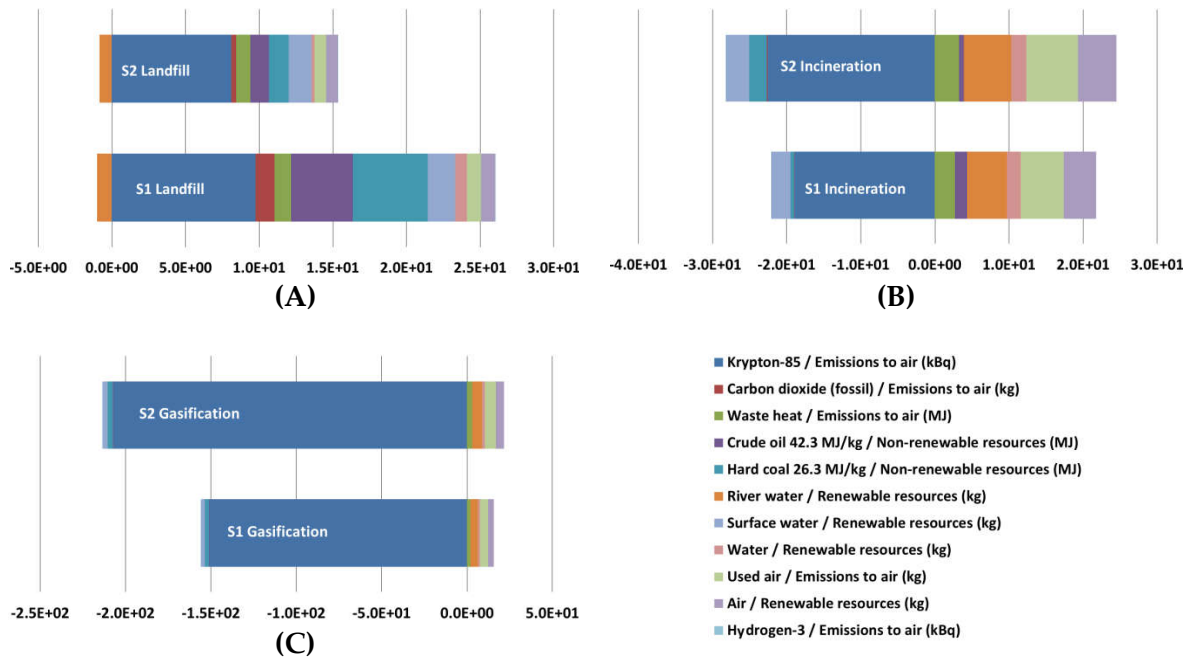


Figure 23. LCI values in disposal phase for the FR cotton curtain with (A) landfill, (B) incineration and (C) gasification as the end-of-life scenarios

From Figure 23, a decrease in LCI values can be seen in a landfill (S2) with eco-design applied as compared to usual landfills (S1) of the FR cotton curtain. The environmental inventory values for the disposal phase depend very much on the scenario: landfills have higher values, while the values for incineration and gasification are lower or even negative due to environmental benefits of energy compensation in valorization. Predominantly, incineration (S2) with eco-design applied has more negative values in contrast to normal incineration (S1) of the FR cotton fabric.

The incineration of textile materials produces energy, saves materials and avoids the undesirable effects of landfilling (methane emissions). From the Ecoinvent database, a generic LCI of textile incineration considers zero carbon dioxide emissions for natural fibers, since carbon dioxide is absorbed during the plant growth (Muthu, 2014), however, cotton curtains are treated with a durable FR product thus carbon dioxide emissions was compensated in both incineration scenarios (S1 & S2) accordingly. Moreover, Ecoinvent calculates the energy recovered as heat and/or electricity from the incineration of one kg natural fibers into 1.36 MJ of heat and 2.86 MJ of electricity (Beton et al., 2014).

6.1.2 LCA results and comparative analysis

6.1.2.1 LCA and comparative analysis of landfill as end-of-life

Figures 24 show a 'cradle-to-grave' comparison of the production, use and disposal phase of 1 kg FR cotton curtain of each of scenario investigated for landfill (S1 & S2). The toxicity categories; FWE, TE, WD and WE are shown in Figure 24 and indicate that the manufacturing phase scores are higher as compared to other phases particularly the use phase.

The impacted categories are related to water toxicity, which is obvious because the textile sector is highly water extensive domain, from the irrigation of raw cotton to final cotton textile (Baydar et al., 2015). Significantly, cultivation of cotton utilizes a considerable amount of fertilizers containing nitrogen and phosphorus chemicals.

While the impact categories; ODP, POCP, and RMD specified the use phase with the higher values, which is highly possible due to higher energy consumptions in use phase since the cotton curtains are washed, dried and ironed for 25 times. Although textile products do not run on energy, they utilize a considerable amount of energy while washing, drying and ironing (Paper II). In addition, the polyester fibers have been shown to consume more energy than cotton (Paper II). Consequently, the production phase of polyester fibers contributes four times more to carbon emissions by utilizing 10 times more energy than cotton (Paper II & III).

The impact values for the distribution phase are insignificant as the distance from the manufacturing country (Turkey) to the use phase country (Italy) is small and transportation has been assumed to be performed by boat.

FRs for textile products are designed to be stable up to high temperatures to protect from fire incidents, consequently are not easily degraded in nature. Such properties of FR substances also exhibit high ecotoxicity, since are they are persistent in the environment. Degradation and removal of these hazardous FR substances would decrease the environmental burdens. A decrease in the environmental impacts after applying the proposed eco-design can be seen in Figure 24B.

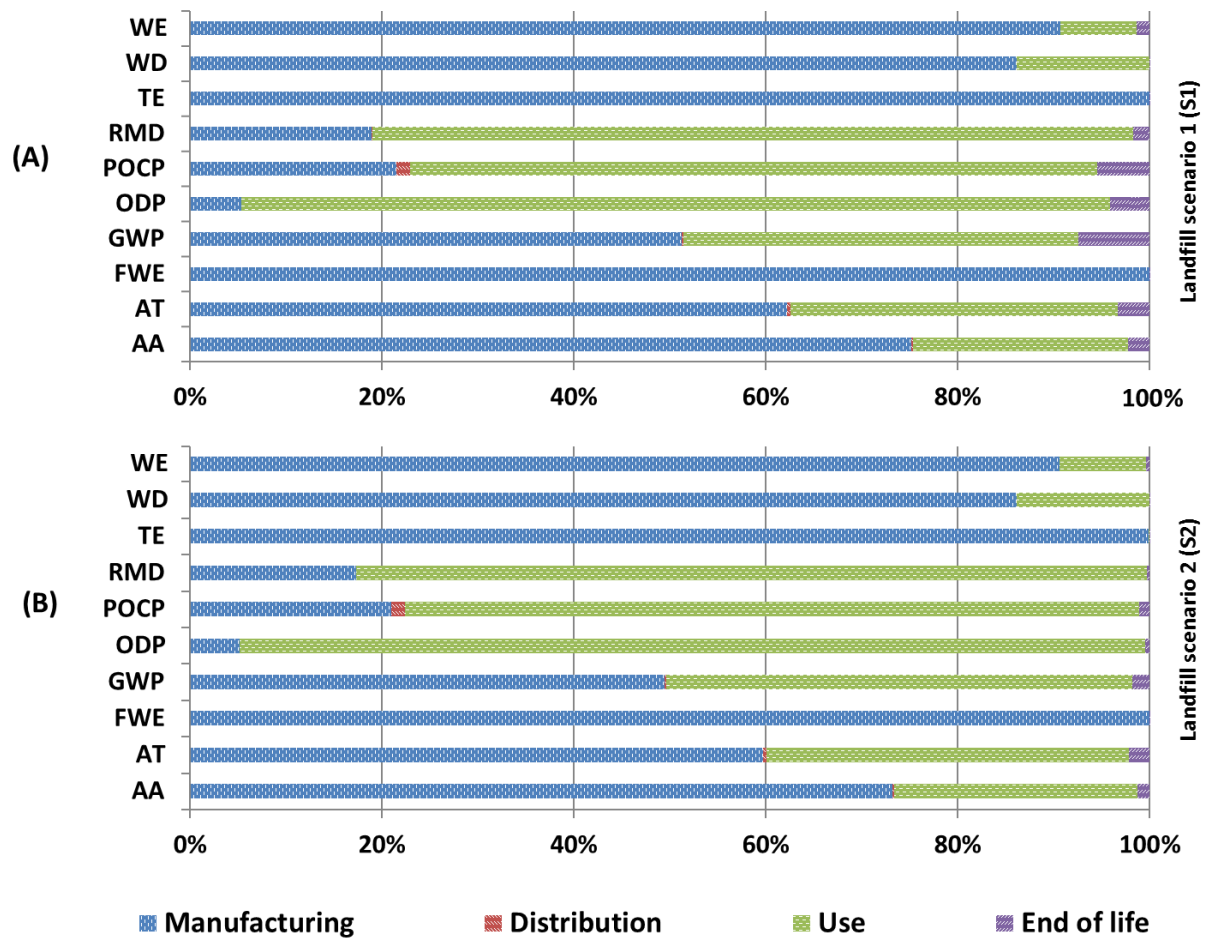


Figure 24. Overall LCA for a FR cotton curtain, cradle-to-grave, (A) for usual landfill scenario 1 (S1) and (B) proposed eco-design landfill scenario 2 (S2) for the toxicity impact categories; Air Acidification (AA), Air Toxicity (AT), Freshwater Ecotoxicity (FWE), Global Warming Potential (GWP), Ozone Depletion Potential (ODP), Photochemical Ozone Creation Potential (POCP), Raw Material Depletion (RMD), Terrestrial Ecotoxicity (TE), Water Depletion (WD) and Water Eutrophication (WE)

A mutual contribution in the impact category GWP can be seen in both landfill scenarios (S1 & S2) by the manufacturing and use phases. The disposal phase also contributes in GWP category since it's a landfill at the end-of-life phase. In Figure 24A, eco-design applied to the FR cotton curtain prior to the landfill, a comparative change can be seen in the impact categories of AA, AT, GWP, ODP, POCP, and RMD. The use phase consisting of 25 laundries has higher GWP, ODP, POCP, RMD scores, which results mainly from the electricity usage for the drying and

ironing. Whereas, the GWP associated with the manufacturing of the FR cotton curtains utilizes fertilizer and pesticide for the cultivation of the cotton.

6.1.2.2 LCA and comparative analysis of incineration as end-of-life

Not so different results can be seen from Figure 25 in the case of incineration as end-of-life of the FR cotton curtain. This is obvious since all the processes are same as for the landfill scenarios except the end-of-life phase. The results also point out that, the manufacturing and use phase of the FR cotton curtain play major roles in generating environmental burden in products life cycle. In incineration, reduced values can be seen in impact categories where landfill showed higher at the end-of-life phase.

Incineration of textile waste is considered rather harmless, although due to some issues to some extent textiles are still landfilled. Although, incineration with energy recovery is more beneficial than landfill but incineration of FR products is rather difficult due to reduced energy recovery and incomplete combustion (Jonkers et al., 2016; Simonson, 2000). Notably, by removing or degrading FR compound from the textile products would ease such hurdles. From Figure 25B, the reduced values of impact categories focusing end-of-life with eco-design applied prior to the incineration can be seen.

An advantage of incineration over landfill at the end-of-life of FR textiles is an evasion of chemical leaching to the environment. Subsequently, FRs can leach from textile products to the environment in the use phase by wearing or abrasion of FRs and end up in indoor dust and land water through sewerage.

In this context, the present work chose to focus on ways to improve the end-of-life phase of FR textile products by degrading and removing the FR substance from the textile. The applied eco-design in scenario S2 prior to incineration was found to give negative values in Figure 25B. It shows more energy recovery with incineration of the FR product after FR substance has been degraded and removed.

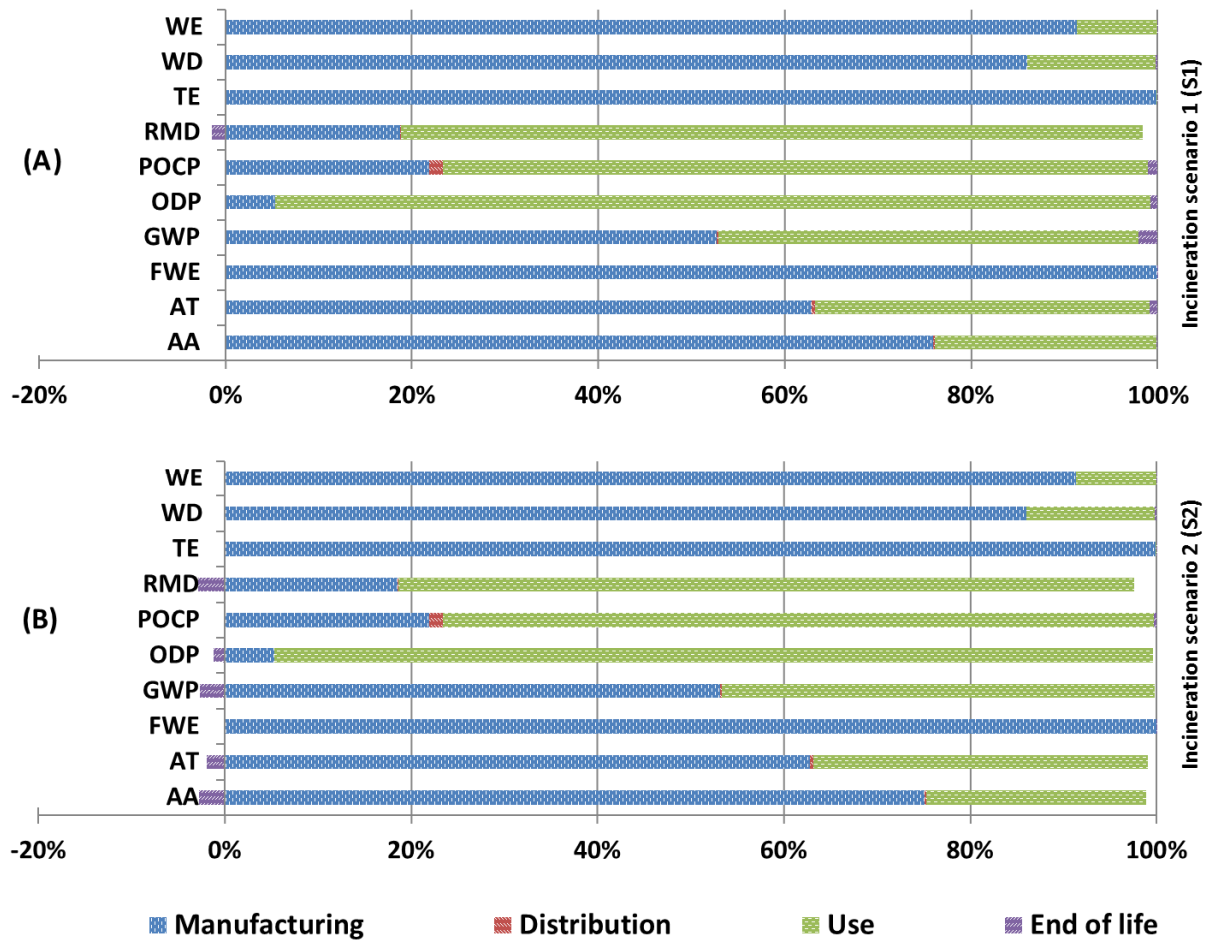


Figure 25. Overall LCA for a FR cotton curtain, cradle-to-grave, (A) for usual incineration scenario 1 (S1) and (B) proposed eco-design incineration scenario 2 (S2) for the toxicity impact categories; Air Acidification (AA), Air Toxicity (AT), Freshwater Ecotoxicity (FWE), Global Warming Potential (GWP), Ozone Depletion Potential (ODP), Photochemical Ozone Creation Potential (POCP), Raw Material Depletion (RMD), Terrestrial Ecotoxicity (TE), Water Depletion (WD) and Water Eutrophication (WE)

The FR textiles function in stopping the flame or fire by producing more char during a combustion process. Consequently, these FR applied to the cotton textiles reduce the energy yield of the cotton in incineration. However, degradation and removal of the FR substances increase the energy yield of the FR treated cotton textiles.

When considering the overall environmental impacts of the FR cotton curtain including the applied eco-design at the end-of-life, we find that scores for the global warming potential, air

toxicity, and acidification, and raw material depletion are decreased significantly, in both the cases of disposals; incineration and landfill.

Scores for FWE, WD, and WE, and TE are not comparable for the excessive water use and chemicals (fertilizers and detergents) in the manufacturing use phases. Whereas, the finishing process of textile products in manufacturing phase on average, consume more or less 1 kg of chemicals and auxiliaries per kg of finished product. The major contributors in generating the environmental impacts in finishing process are salts, detergents and organic acids (Turunen and van der Werf, 2006).

It is important to discuss the contributor with second most impact values, the use phase. From the results of use phase in Figure 24 and Figure 25, we can conclude that cotton textile products require a high amount of energy for washing, drying, and ironing (Paper II). Cotton fiber products are heavier in mass weight, which evidently increases the washing load (Dahllöf, 2004). Moreover, the cotton fiber products absorb more water; consequently, more water is required for washing and more energy for heating the water (Finnveden et al., 2005).

6.1.2.3 LCA and comparative analysis of gasification as end-of-life

Similarly, for gasification in the disposal phase system expansion was considered, in which energy is recovered for electricity production and district heating, replacing fossil fuels that are usually utilized during the production of electricity and heat for the textile industry. The recovered energy from the gasification of FR textiles is accredited to the product system in LCA software used.

The inverted average developments from evolved syngas from the gasification is considered for the electricity production and heating in the model. This way the benefits from the reduced use of fossil fuels are taken into consideration.

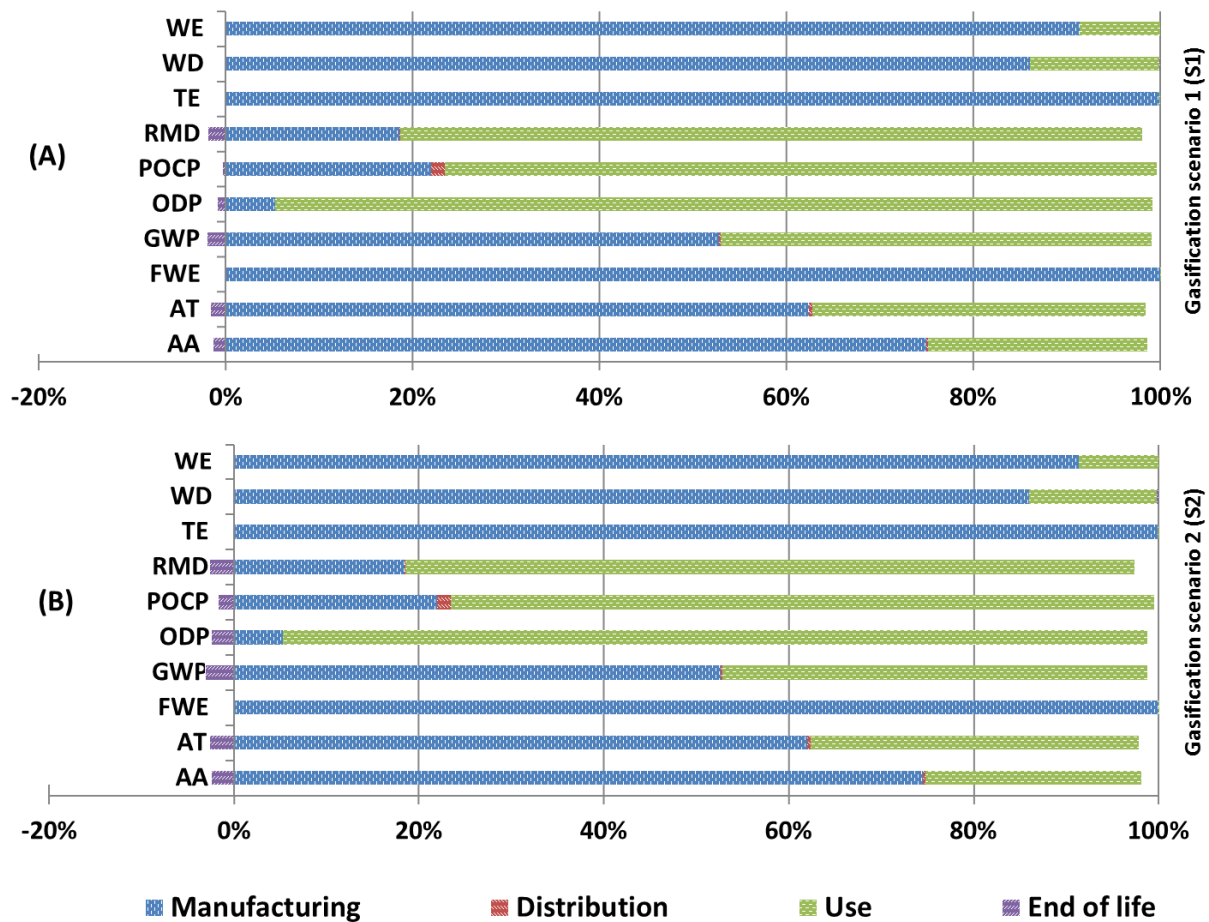


Figure 26. Overall LCA for a FR cotton curtain, cradle-to-grave, (A) for gasification scenario 1 (S1) and (B) proposed eco-design gasification scenario 2 (S2) for the toxicity impact categories; Air Acidification (AA), Air Toxicity (AT), Freshwater Ecotoxicity (FWE), Global Warming Potential (GWP), Ozone Depletion Potential (ODP), Photochemical Ozone Creation Potential (POCP), Raw Material Depletion (RMD), Terrestrial Ecotoxicity (TE), Water Depletion (WD) and Water Eutrophication (WE)

The Figure 26 shows the impact categories of the FR cotton curtain disposed of in the gasifier. The benefits from the reduced use of fossil fuels in the manufacturing phase are visible. In the gasification scenario 1 (S1) in Figure 26A, the considerations are taken into in the favor of energy recovery and syngas produced from the gasification of FR textiles, in the impact categories of RMD, GWP, and AA compared to the incineration scenario (S1). It is obvious since more credit is allocated for the generation of syngas from gasification instead of energy recovery from heat generation from incineration.

In contrast to gasification scenario 1 (S1), gasification scenario 2 (S2) showed decreased impact values in the RMD, GWP and AA categories. In addition, more negative values are visible for the end-of-life phase of the FR curtain being gasified for scenario 2 (S2).

6.2 Characterization results of end-of-life scenarios

6.2.1 End-of-life analysis for landfill

As mentioned earlier, the environmental impact values in the end-of-life phase have only a small contribution to the overall impact over the complete life cycle of the FR cotton curtain, however, this phase could pose serious threats to the environment (ENFIRO, 2009). To find the effects of optimized end-of-life phases for the landfill and incineration, the distinctive analysis was necessary even with the fractional impact values.

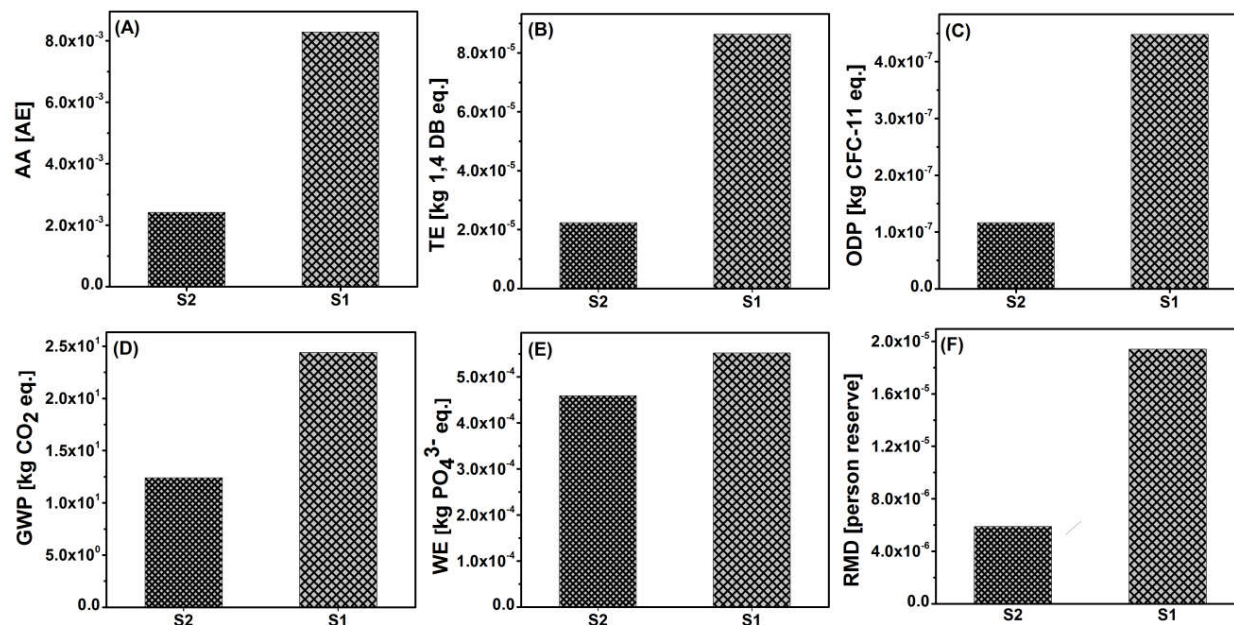


Figure 27. End-of-life analysis of usual landfill (S1) and with eco-design applied landfill (S2) scenarios, for the impact indicators; (A) Air Acidification (AA), (B) Terrestrial Ecotoxicity (TE), (C) Ozone Depletion Potential (ODP), (D) Global Warming Potential (GWP), (E) Water Eutrophication (WE) and (F) Raw Material Depletion (RMD)

The end-of-life impact values for usual landfill scenario S1 was compared with eco-design applied landfill scenario S2 in Figure 27, and S2 showed lower contribution on each of the

impact categories. The main differences between the two end-of-life phases as landfill scenarios are found for the impact categories AA, TE, ODP, RMD and GWP, as shown in Figure 27 (A, B, C, D and F). For the other impact category, the impact value of WE for S2 is not so different from S1 (see Figure 27E).

6.2.2 End-of-life analysis for incineration

Impacts of the incineration scenarios show a different profile to those of landfill scenarios at the end-of-life phase. Figure 28 show results for usual incineration compared to the FR cotton curtains gone through eco-design and incinerated at the end. The studied impact categories for incineration scenario (S2) are comparatively lower than the usual incineration scenario (S1). A relatively low and negative value of the impact indicators for (S2) like air acidification, ozone depletion, and global warming climate shows the elevating environmental impacts of eco-design for FR cotton curtains.

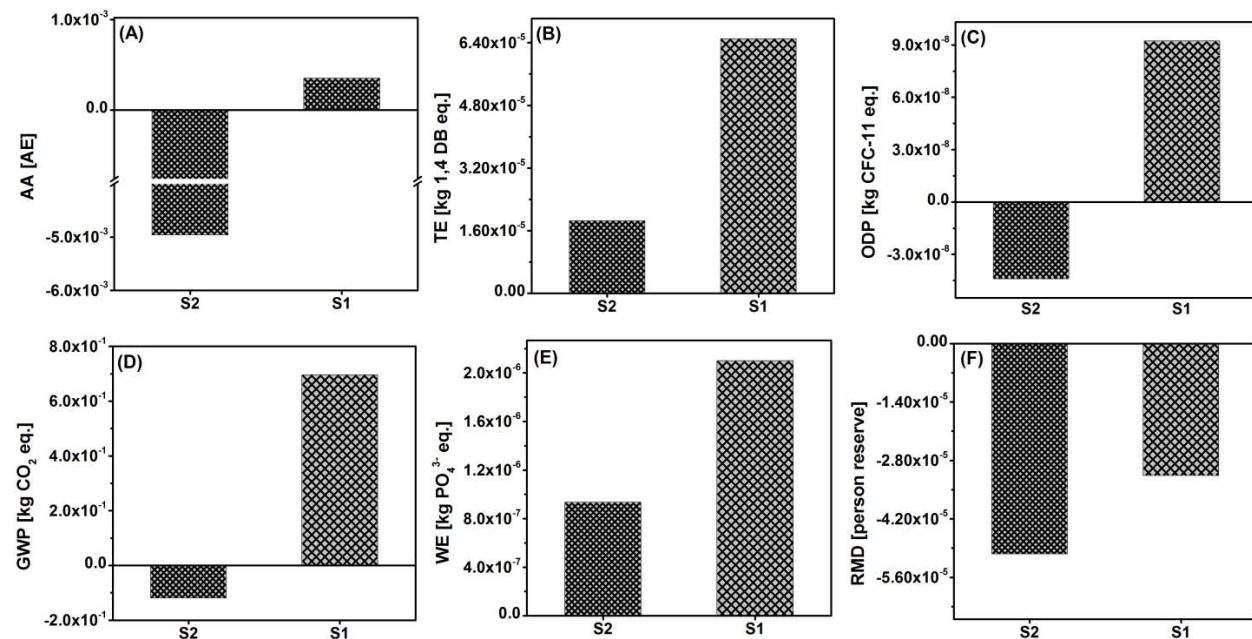


Figure 28. End-of-life analysis of usual incineration (S1) and with eco-design applied incineration (S2) scenarios, for the impact indicators; (A) Air Acidification (AA), (B) Terrestrial Ecotoxicity (TE), (C) Ozone Depletion Potential (ODP), (D) Global Warming Potential (GWP), (E) Water Eutrophication (WE) and (F) Raw Material Depletion (RMD)

6.2.3 End-of-life analysis for gasification

Figure 29 illustrates the comparison of gasification scenarios (S1 and S2). The system expansion applied for gasification scenario 2 (S2) calculates the net primary energy usage as a credit and greenhouse gas emissions as neutral or in negative. The result of gasification scenario 1 (S1) in the end-of-life is obvious in negative values, suggesting limited emissions at disposal. In an alternative to gasification scenario 1 (S1), gasification scenario 2 (S2) gave extra negative values after the eco-design applied.

The FR substance on the textile makes it difficult to have an oxidation reaction and leads to incomplete combustion. The degradation of FR substance from the textiles helps in having a better oxidation in the gasification process, consequently, produces syngas with improved contents in the end.

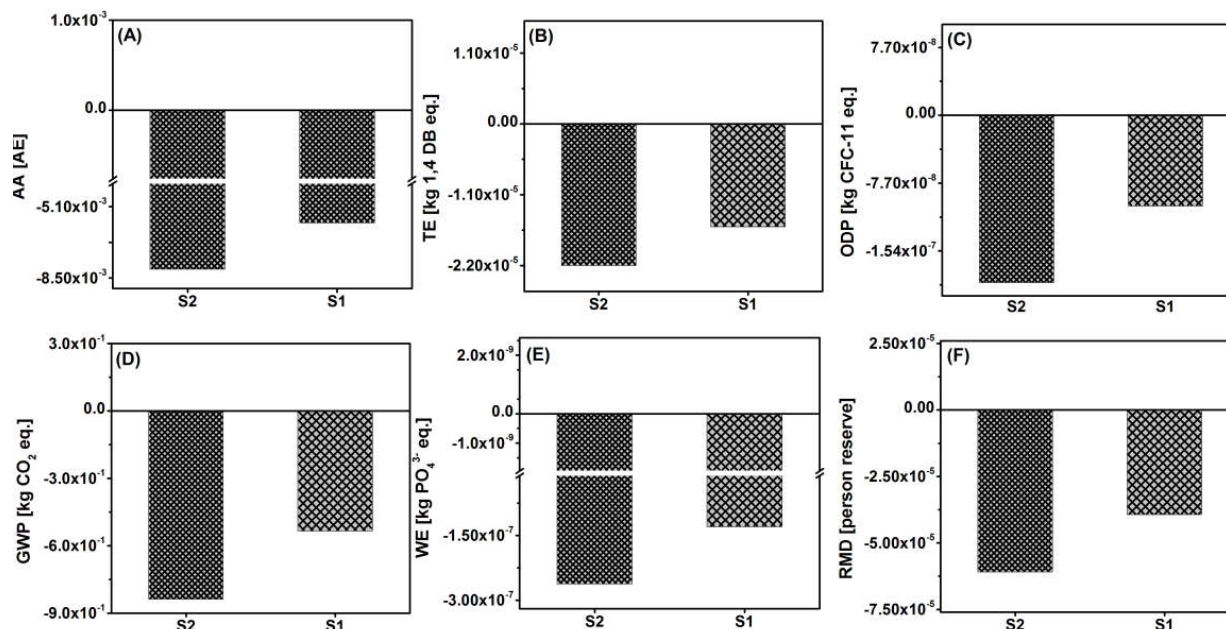


Figure 29. End-of-life analysis of gasification (S1) and with eco-design applied gasification (S2) scenarios, for the impact indicators; (A) Air Acidification (AA), (B) Terrestrial Ecotoxicity (TE), (C) Ozone Depletion Potential (ODP), (D) Global Warming Potential (GWP), (E) Water Eutrophication (WE) and (F) Raw Material Depletion (RMD)

6.3 General discussion

Aforementioned, the FR substances from the textile products can be released to the environment in different pathways, for instance, production, processing, use, and disposals. It is

extremely difficult to determine or estimate the release of the FR substance in a textile product at each phase of its lifecycle (Nazaré, 2009). Furthermore, the FR textiles are not branded as hazardous substances, since are used to reduce the risks in fire situations. Thus FR textiles are disposed as municipal waste and not as hazardous waste (Cefic and EFRA, 2006), and finally, end up at landfilling or incineration.

Landfill of FR has detrimental environmental effects of FR chemical leaching and landfill gas, while incineration is linked to emissions and generation of undesirable toxic products. Despite the fact that landfilling and incineration have their limitations, no sustainable alternative procedure is available to dispose of textile products, especially FR textiles. Recycling/reuse of textile products are highly encouraged by researchers, NGOs, and governments, yet are rare to be found practiced or textile products eventually end at incinerators and landfilling after reuse/recycling. However, degradation and removal of permanent/durable FR product from the textile products prior to their disposals has been found beneficial in lowering the environmental burdens from cradle-to-grave LCA.

In the landfill scenarios, the environmental impact categories GWP and ODP have been reduced almost by 51% in the end-of-life phase after eco-design being applied (S2) before landfills (degradation and removal of FR product). Similarly, a decrease in other indicators, for instance, 26% in WE, 31% in AT and AMD, and 43% in TE was found compared to usual landfill scenarios (S1). Although incineration of natural textile products is considered more or less predominantly not detrimental, FR substance on the textile product may pose certain environmental threats. Degradation and removal of the FR product prior to the incineration of FR textile products was also found positive in lowering the environmental burdens. A significant reduction was seen in the ozone depletion potential for eco-design incineration scenario (S2) which was 48% lower than the usual incineration scenario (S1). Likewise for other indicators a reduction of 45% in WE, 17% in GWP, and relatively lower reduction in AA, AT were observed.

Notably, energy recovery from incineration of textile products differs from fiber to fiber. For instance, energy recovery from incineration of 1-ton cotton can recover 28%, while polyester

recovers around 15% energy (Finnveden et al., 2005). Accordingly, the energy recovery from the FR cotton would be lower due to an incomplete combustion of textile materials during incineration. Degradation and removal of a FR substance from the textile products, for instance, pure cotton and cotton/polyester blends, would be an optimized step to increase the energy recovery for valorization.

The Fenton's reagents used in the eco-design treatment are excluded in the overall LCA values since the post effects of the reagents were assumed neutral. The Fenton's reagents are known as an oxidizing process for destroying hazardous organics and are applied to treat a range of wastes associated with the textile industry and chemical manufacturing. Moreover, leaching of the FR during the landfill was excluded, due to lack of data, which certainly affects the toxicity outcomes.

The incineration perspective of oil combustion replacement would lead to more negative emission values of carbon dioxide and sulfur oxides. However, only one system expansion from the incineration of textile products was measured in this study. The aspect of system expansion as heat recovery and its possible emissions from the incineration were taken into consideration.

An overall comparison of the FR cotton curtain with usual landfill and incineration disposals, and with applied eco-design disposal scenarios are shown in Figure 27 and 28. The differences are minute, since, the end-of-life has a very small contribution to overall environmental impacts in both the cases but the disposal scenarios with eco-design applied are comparative enough with the usual disposals. Though all scenarios have the same manufacturing and washing processes, the end-of-life phase is different. One consequence is that the manufacturing phase dominates more than the other phases of the studied impact categories.

Namely, the indicators with altered LCA values after eco-design being applied are AA, FWE, GWP, ODP in both disposal cases. In the incineration scenario (S2), the most reduced values are of the air toxicity compared to incineration scenario (S1), which is possibly due to an increase in combustion properties after FR being removed. The indicators got least affected from the eco-

design in both disposals are TE, WD, and WE. These indicators are often dominated by the manufacturing phase.

The lower environmental values for the incineration scenario as end-of-life phase are taken as an environmental benefit for the recovered heat from the combustion of FR cotton curtains, which is not the case in the landfill. Clearly, eco-design applied to scenarios of incineration and landfill end-of-life is in favor for the indicators responsible for the impacts at disposals.

To determine from the environmental impact values, landfill does not appear as a very good disposal phase for FR textiles even prior to the degradation of a FR substance. Alternative to landfill, incineration has benefits with both scenarios of with and without the eco-design applied (degradation of FR substance). Moreover, the gasification of FR textiles after the eco-design applied showed lower impact values suggesting benefits of gasification.

6.3.1 Recycling alternatives for FR textiles

However, recycling of FR textiles were not the main aspects of the thesis, an initiative study was carried out to explore the recycling possibilities at their early disposals. In the literature, various evidences on the environmental benefits can be found on textile recycling and reuse as second-hand textiles where no reprocessing is involved. Recycling of FR textiles into other materials is rather difficult to find in practice (Paper III). The reason is given as a lack of advancement in textile recycling and accessibility of cheap fabrics in markets. However, durable FR textile products, such as curtains which are washed 15-25 times in their lifespan, still maintain their FR properties at disposal (Conference paper I), can be recycled into other useful materials.

A preliminary study was carried out to deal with the possible recycling of FR-treated cotton curtains, instead of being disposed for landfill or valorization. Mechanical recycling technique of FR textiles was employed and CO₂ emissions were calculated for preliminary studies. The organophosphorus FR MDPA treated cotton curtain was considered to be mechanically recycled into FR insulations at the end-of-life phase rather being landfilled or valorized (Paper III).

Even though a number of assumptions were made due to the lack of available data regarding energy usage within the processes of FR cotton/polyester insulation and FR curtain production, a great reduction in carbon footprint is obvious when virgin production is avoided. Although the calculated values of carbon emissions were incomplete, the analysis of mechanical recycling of FR cotton curtains highlights the recycling possibilities of FR textiles into other useful materials at their disposal (Paper III). The recycling of FR textiles is considered beneficial, however even the recycled FR products ends up at landfill or incineration, which later on requires eco-designing.

Chapter 7

Conclusions and perspectives

7.1. Conclusions

This Ph.D. work aims at generating a comprehensive focus on the end-of-life phase of textile products, especially cellulosic materials with durable FRs.

The entire work can be divided into four partitions:

1. Evaluation of ecological issues and proposing an eco-design for the end-of-life phase
2. A pragmatic degradation of FR species for eco-design of end-of-life phase
3. Energy valorization of FR textiles through gasification
4. Comprehensive LCA of the proposed eco-design and gasification

1. Evaluation of issues and eco-designing

The most practiced solution of textile waste at its end-of-life, up to now has been landfilling and incineration with low energy recovery in the end. Though, the waste of textile products represents an important environmental issue with both landfilling and incineration, especially FR textile products. To explicit, incineration is not considered sustainable for a reason of generating emissions and ashes in the end. Consequently, the landfill is undesirably adopted but is feared of landfill gas, leachate, and land shortage for the disposals, since every country will eventually run out of landfill space. The disposal of textile products with FRs is more environmentally severe than the ones without. It was quickly concluded that there is an urgent need of sustainable path for the end-of-life phase of textile products or eco-designing of their disposals. To cope with such issues and considering the environmental urgency, an eco-design was proposed with optimized disposals for the FR textiles. Eco-design comprises of the degradation and removal of a permanent/durable FR substance from the textiles, especially cellulosic textiles prior to their disposals.

2. Degradation of flame retardant species

For the degradation of FR species, the results of this study show that the Fenton's reaction can be effectively used for the degradation of the durable/permanent organophosphorus FR (MDPA and TMM) both in aqueous media and after binding to the cotton fabrics. Degradation or removal of the FR substance from the textile products can be a suitable pathway to decrease environmental impacts in the end-of-life of textiles and other possible re-usability.

For energy production by incineration, the increase in heat release rate of Fenton's reaction degraded FR cotton fabric can be interesting as compared to FR cotton fabrics. From the thermal study of the cellulosic fabric after the degradation of FR species, the heat release rate (HRR) has been increased by 51% compared to the FR treated ones. Moreover, the cellulosic fabrics show unchanged mechanical properties after having gone through the highly oxidative Fenton's reaction, which is due to the time-limited reactions and the nullifying effect of Fenton's reagents by strong alkaline solutions.

The re-use of the degraded FR cotton textile for many applications is possible, for instance, geo and agro textiles. It was decided to carry further studies to enhance the energy valorization of FR textiles after the degradation of a FR substance during the incineration or gasification process. An LCA study to confirm the advantages of using the Fenton's reaction at the end-of-life of FR cotton textiles was also taken into considerations.

3. Energy valorization by gasification

Waste of textile products represents an important environmental issue, especially FR textile products. The most practiced solution up to now has been landfilling and incineration with low energy recovery is less preferred. However, such wastes have a chemical potential, as they can change into a medium heating value syngas. A gas consists of essential components for the production of fuel or chemical intermediates, such as hydrogen, methane, and carbon monoxide.

There is a concern of low energy yield and toxic emissions during the incineration of FR textile products, which led to a huge gap in literature especially on the disposal of such high-performance textiles. However, as an alternative, the degradation, and removal of FR species from textile products prior to their disposal can overcome such challenges. After the degradation of permanent/durable FR substance from the cotton textiles with the oxidation method (Fenton's reaction), making it suitable for the gasification process as a biomass. Considering the gasification temperature, preliminary results suggest that the prepared pellets of FR textiles after the degradation and removal of FR substance can reach the reaction parameters of the gasification. Moreover, the average temperature was higher for the FR cotton after the degradation and elimination of FR substance, since the removal of FR substance has improved the combustion/gasification properties of the cotton textiles.

The incineration is the environmental technology of controlled combustion with the recovery of heat to produce steam and eventually electricity. However, incomplete combustion of waste releases toxic chemicals, such as lead and mercury, and additional byproducts. Whereas, incineration and gasification processes can be compared in terms of energy recovery. For incineration, FR degradation increases the HRR by more than 50%. However, prior FR degradation, gasification is more interesting since there are no toxic fumes compared to incineration. Indeed, in gasification FR on textiles are also gasified: degradation of FR from textiles gives slightly higher energetic yields by improved combustion.

4. Comprehensive LCA of the eco-design

From the LCA, a comparison of overall environmental impacts of three end-of-life phase scenarios for FR cotton textiles. One end-of-life phase with usual and applied eco-design landfill was demonstrated, while the second end-of-life phase deals with the usual and applied eco-design incineration of FR cotton textiles. The third deals with the gasification of the FR cotton textiles before and after the degradation of FR species with proposed eco-design.

Due to low contributions to an overall cradle-to-grave LCA scores, end-of-life phases are often ignored. This study not only shows the importance of this phase but also provides alternatives

to optimize the end-of-life phase. The relatively low environmental impact results of the applied eco-design as modeled in the study show a potential significance of end-of-life phase.

The environmental impact categories, such as GWP and POCP were found to be reduced almost by 51% in the end-of-life phase after degradation and elimination of the FR substance in landfill scenarios (S2). Similarly, a decrease in other indicators, for instance, 26% in terrestrial ecotoxicity, 31% in air toxicity and raw material depletion, and 43% in water depletion was found compared to usual landfill scenarios (S1).

In incineration scenarios, a significant reduction was seen in ODP of incineration scenario (S2) which was 48% lower than the usual incineration scenario (S1). Likewise, for other indicators, a reduction of 45% in WE, 17% in GWP, and relatively lower in AA, and AT impact categories was seen.

Since the combustion properties were found to be improved with the degradation and elimination of the FR substance, energy valorization by gasification was also found to be enhanced. In the gasification scenarios, a 27% decrease was seen in impact values of GWP and ODP for the gasification scenario 2 (S2). Moreover, the 34% in AA and more than 50% decrease in RMD impact values were observed after the degradation and elimination of a FR substance from the cotton textiles.

7.2. Reuse and recycling of FR textiles

Reuse/recycling of the FR cotton textiles after eco-design applied was not amongst the studied interventions in the present study. Although degradation and elimination of FR species or substance from the cotton fabrics with AOP was found successful, retaining the mechanical properties of the fabric. Optimal degradation and removal of FR species from the textiles are possible by increasing the AOP measures and concentrations. The FR textile products after the degradation and removal of FR species can potentially be used for agro and geotextiles. However, it is important to extensively study the impacts of reuse and recycling of FR textiles, as numerous recycling technologies are under development. The environmental potentials can be estimated by reusing and recycling processes in comparison with conventional landfilling

and incineration with and without energy recovery. For instance, FR textiles can be used for FR insulation panels with mechanical recycling process. Also, as aforementioned, reusing FR textiles as agro and geotextiles after degradation and removal of FR species would bypass the production of virgin textiles.

7.3. Future perspectives

The degradation of the FR can be enhanced by using various reaction combinations, for instance, Fenton's reactions with different pH solution and reaction temperatures, Fenton-like reactions, and UV-Fenton etc. Moreover, it would be interesting to see the possibilities of degradation and mineralization with other oxidation-reduction technologies and enzymatic treatments.

The incineration of biomass such as cotton produces ash and other residues. Theoretically, the bottom ash or tar is approximately 20-30% by weight of the waste input, while the fumes or fly ash is lower 3-6% of the input. The perspective of degradation and removal of FR species from the fabric led to better combustion than the one without being degraded or removed. However, with better residue filtration and cleaning of the exteriors particles, the outcomes would be different.

The expected uncertainties are to occur in this study due to lack of descriptive data for the end-of-life phase of textiles, especially FR textile products. The primary life cycle inventory data for the degradation and removal of FR species or substance from the fabric came from preliminary experimental results. Besides the amount of leftover FR species or substance and particulates after the AOP reaction on the fabric should be addressed in future work. Moreover, the wearing off or abrasion and volatilization of FR at the end-of-life phase should be considered. This would allow a more comprehensive insight on the FR species or substance quantity going into the disposals and its associated environmental impacts.

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