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Project Report

When Physical Chemistry Meets Circular Economy to Solve Environmental Issues: How the ReScA Project Aims at Using Waste Pyrolysis Products to Improve and Rejuvenate Bitumens

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Abstract: Urban waste management is a hard task: more than 30% of the world's total production of Municipal Solid Wastes (MSW) is not adequately handled, with landfilling remaining as a common practice. Another source of wastes is the road pavement industry: with a service life of about 10–15 years, asphalts become stiff, susceptible to cracks, and therefore no longer adapted for road paving, so they become wastes. To simultaneously solve these problems, a circular economy-based approach is proposed by the ReScA project, suggesting the use of pyrolysis to treat MSW (or its fractions as Refuse Derived Fuels, RDFs), whose residues (oil and char) can be used as added-value ingredients for the asphalt cycle. Char can be used to prepare better performing and durable asphalts, and oil can be used to regenerate exhaust asphalts, avoiding their landfilling. The proposed approach provides a different and more useful pathway in the end-of-waste (EoW) cycle of urban wastes. This proof of concept is suggested by the following two observations: (i) char is made up by carbonaceous particles highly compatible with the organic nature of bitumens, so its addition can reinforce the overall bitumen structure, increasing its mechanical properties and slowing down the molecular kinetics of its aging process; (ii) oil is rich in hydrocarbons, so it can enrich the poor fraction of the maltene phase in exhaust asphalts. These hypotheses have been proved by testing the residues derived from the pyrolysis of RDFs for the improvement of mechanical characteristics of a representative bitumen sample and its regeneration after aging. The proposed approach is suggested by the physico-chemical study of the materials involved, and aims to show how the chemical knowledge of complex systems, like bituminous materials, can help in solving environmental issues. We hope that this approach will be considered as a model method for the future.

Keywords: char; pyrolysis; circular economy; waste disposal; anti-aging; bitumen; rejuvenator; bio-oil; end-of-waste

1. Introduction

Around 2.01 billion tons of municipal solid waste (MSW) are produced worldwide each year, of which 33% are not adequately handled [1]; in many countries, indeed, the urban wastes (household, school, industrial, hospital wastes, etc. [2]) are still treated by processes lacking in re-utilization or recycling activities. Improper solid waste management practices produce social and economic problems, have significant environmental repercussions, and increase human health risks [1].

Looking at Europe, in 2019, 224.4 million tons of MSW were produced, of which 31% was recycled, 27% was converted into energy, 18% underwent biological treatments, 24% was dumped into a landfill, and 1% was incinerated. In Italy, the percentages of waste treatment are in line with the European trend, but in comparison with German, it was noted that a better waste management process is feasible (Italian vs. German percentages: recycled 33% vs. 48%; energy recovery 21% vs. 32%, biological treatments 23% vs. 18%, landfilling 23% vs. 1%, incineration 1% vs. 1%, respectively) [3].

The disposal to landfills has the following consequences:

- country landscape disfiguring;
- maintenance and transport costs [4], since landfills are often located in remote areas;
- health problems due to the proliferation of bacteria and insects [5];
- pollution of soil, groundwater (due to percolation of liquids from organic matter decomposition), and atmosphere (emission of gaseous decomposition products [6] such as methane, which is twenty times more harmful than CO_2 as a greenhouse gas [7]).

Thermochemical conversion processes (pyrolysis, gasification, combustion or incineration) are convenient strategies to produce fuel and energy from MSW [8]. The amount of MSW for thermal treatment reached 921 kton/yr in 2010–2015 [8]. Unfortunately, the combustion and incineration of waste have a non-negligible environmental impact [9–11]. The target of thermal treatment, indeed, should be to provide for an overall reduction in the environmental impact that might arise from improper waste management.

The pyrolysis process for waste transformation [8] is performed in the absence of O_2 in specifically designed reactors, under specific temperatures and pressures, allowing for: (i) the production of three added-value products (bio-oil, gas, and char) [8,12–14]; (ii) a higher energy recovery efficiency, and (iii) the reduction of polluting gaseous emissions [15].

Although there are undisputed advantages for the use of this specific thermochemical process [8,16], and no significant increase in terms of CO_2 emissions occurs, the economic returns associated with the condensable fraction (bio-oil) and solid product (char) are not completely defined because:

- bio-oil is a complex liquid mixture containing hydrocarbons and oxygenated species with a very wide variety of molecular weights, which are still difficult to exploit and make use of;
- char is a solid carbon-based material with a high inorganic fraction (depending on the feedstock) that limits its functional exploitation.

Another cycle that is still open in several countries is the asphalt cycle. After ~10–15 years, asphalts become aged, and hence hard and fragile, and are no longer suitable for road paving, so they are replaced with new ones, since expensive chemical treatments are needed for their regeneration. Recently, governments and road authorities demanded that the pavement industry became more sustainable by reducing the consumption of both costly virgin and increasingly scarce materials and avoiding landfilling. In Italy, like other EU countries, only 20–30% of reclaimed asphalts are reused for new paving processes, and 8–10 wt.% of the available reclaimed asphalts were landfilled in 2018 [17,18]. The re-use of removed asphalt can significantly reduce the overall costs of new road paving materials [18,19]. The use of waste materials in road applications can also help in cost reduction, and an increasing trend for their use for such a scope can be found [20].

In the present work, a virtuous pathway for the utilization of pyrolysis-derived residues to improve asphalt performances and increase their life-cycle, thus reducing disposal to landfills, is proposed. The feasibility of this idea is witnessed by the recent financing of a research project (ReScA) aiming at an advantageous use of both solid (char) and liquid (bio-oil) products derived from the pyrolysis of wastes to produce more durable and highly performing bitumens and asphalts, thus guaranteeing greater road safety and lower waste production.

This work is organized as follows: first, the physico-chemical basis underlying the idea of using pyrolysis-derived residues to improve the asphalts characteristics is introduced (Section 2), then the feasibility of the approach, as well as the methodology and the work carried out so far under the ReScA project, are reported in Sections 3 and 4, the expected impacts in technological, social, and economic fields are reported in Section 5, and the conclusions, together with some final comments on future perspectives, are reported in Section 6.

2. The Physico-Chemical Basis for the Integration of Wastes and Asphalt Cycles

Polymers are common additives for the improvement of asphalt properties, but up to now, their use has been uneconomical due to their high cost [20]. Recent research advances demonstrated the possible use of wastes, or products derived from the pyrolysis of wastes, as emerging bitumen and asphalt additives [20–24]. In addition, recently, the physico-chemical bases of the improvement of asphalt mechanical characteristics due to char addition have been assessed [25–30]. Char exhibits antioxidant and anti-aging properties when used as an asphalt additive, and bio-oil can exert regenerative properties on aged asphalts, restoring the maltene phase with low-molecular weight molecules [27,31].

Nano-sized particles, thanks to their high surface-to-volume ratio and tuneable chemical composition, can exert a significant effect on the rheological properties of bitumens and asphalts, even when added to bitumen in very small percentages [32]. In particular, fine particles are able to increase the load capacity of the pavement and decrease the formation of cracks due to fatigue during the pavement's operation life. Carbonaceous particles are expected to give better results, thanks to their chemical compatibility with the bitumen (they are both carbon-rich materials) [25]. The char, being characterized by a porous and fibrous structure, is responsible for strong interactions with the binder [28]. In addition, its high carbon content has been found to affect bitumen hardness and toughness [33]. The use of char as a bitumen modifier has been tested by different authors [34,35] and in all the cases, improved mechanical performances were detected.

The interactions between char and bitumens can also have anti-aging effects. The chemical reasoning supporting this hypothesis is that the interaction of the apolar part of the char with the maltenic phase of bitumen is expected to constrain the latter into more restricted dynamics. Therefore, the presence of solid particles like char, hindering bitumen transformation dynamics, could slow down the processes responsible for aging, including the dynamics involving asphaltene clusters and their aggregates, at different length scales and interacting with different strengths [36].

Very recently, Rajib et al. in 2021 [37] examined the benefits of using biochar to delay oxidation and UV aging on both binder and asphalt, and Kumar et al. [38] evaluated the thermal storage stability of binders modified with pyrolyzed plastic waste (PPC). Their work demonstrated that the pyrolysis residues can be used as modifiers in bitumens, but it emerges that much work is still needed, in particular to face stability problems [38].

Under aging, cracks or fractures in asphalt can take place [39], since bitumen chemical components become less and less mobile under the applied stress. Aging is the overall result of several processes, each of them characterized by their own timescales:

1. volatilization of lighter components [40], a phenomenon occurring even during new asphalt placement [41,42];
2. oxidation of bitumen constituents by atmospheric oxygen. Oxidized molecules are more polar and can give enhanced self-assembly [43];
3. chemical reactions causing polymerization and formation of larger structures within the bitumen (thixotropy) [44].

After aging, the bitumen's original ductility/viscosity can be somehow restored by the simple addition of softening (usually called fluxing) agents, such as flux oil, soy oil, slurry oil, lube stock, etc. [45,46].

To date, more sophisticated methods to restore the original chemistry of the neat bitumen and its original inter-molecular structure [36,47] (rejuvenation) by delaying the oxidations, agglomerations, and self-assembly processes occurring during the whole aging process have been formulated.

Regarding the use of bio-oil, it has been proven that its composition makes it a possible fluxing agent. The rationale behind this application lies in the presence of amphiphilic molecules that can interact with those already present in the bitumen. The interaction between different types of amphiphilic sites can be various, due to the complex nature of such molecules, and with marked effects, especially if acidic and basic molecules come into contact within the system, due to a favourable energetic push towards strong H-bond formation or, even a definite proton transfer with the formation of charged species [48]. In this framework, a recent example is offered by the work of Ren et al. in 2020 [49], where the addition of bio-oil derived from biomass pyrolysis to bitumen has been tested to improve its performance. The improved bitumen was applied to self-adhesive and doped hot-melt sheets. Bio-oil was tested by FT-IR, by GC-MS and by Karl Fischer titration, whereas the bitumen performances were evaluated by softening point tests, low temperature flexibility tests, peeling strength tests, viscosity, density, hardness and heat resistance determinations, and maintained stickiness tests. Results on physical properties evaluation demonstrate that bio-bitumen is a potential substitute in bitumen coating sheets.

In the next section, details about how these aspects are exploited and further analysed within the ReScA project are reported.

3. Methodology and Preliminary Results: The ReScA Project

The ReScA project focuses on the feasible utilization of both bio-oil and char from pyrolysis processes to produce better and longer-lasting asphalts, as well as to regenerate them on-site once they are aged or exhausted. The ultimate goal of ReScA is the integration of urban wastes and the asphalt cycles. It will be accomplished according to two main pillars (Figure 1): (i) the tuning of the pyrolysis product characteristics through process optimization; (ii) the use of pyrolysis products for asphalt formulation and rejuvenation when they are aged or exhausted.

The proposed approach leads to the following general benefits:

1. replacement of petroleum-derived products (e.g., crude oil) with products from the pyrolysis of urban solid wastes;
2. improvement of the mechanical characteristics and the longevity of asphalts through the use of char;
3. low-cost and on-site rejuvenation of exhausted asphalts through bio-oil.

The above-mentioned benefits are expected to greatly impact aged asphalts disposal in landfills, CO_2 emission, and production costs, as a consequence of the increased asphalts duration. Moreover, the ReScA concept, adopting the exploitation of pyrolysis from the transformation of urban wastes (focusing on refuse derived fuels, RDFs), at the same time, allows for a significant energy recovery [50] (the heating value is typically around 20 MJ/kg [51]) and the reduction of landfilling, accomplishing the circular economy paradigm which is urged to be adopted in the post-COVID-19 transition.

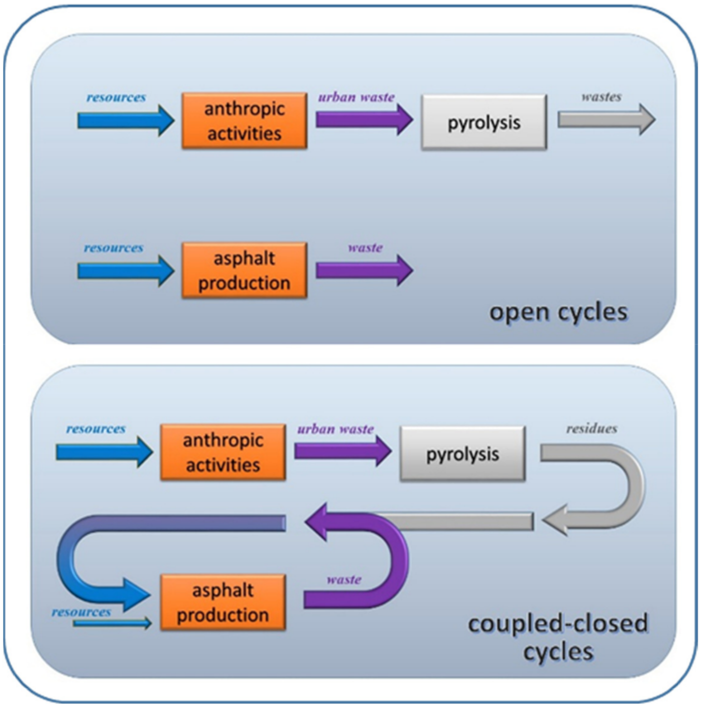

Figure 1. Scheme representing the ReScA concept for the integration of pyrolysis and pavement production cycles.

3.1. Methodology (Pyrolysis, Rheological Properties of Asphalts)

ReScA pursues an unconventional exploitation of solid and liquid products (char and bio-oil) for the thermoconversion of urban waste to enhance and improve asphalts, making them more resistant and long-lived (through the use of char) and allowing for their on-site regeneration through the use of bio-oil. ReScA is an interdisciplinary project taking advantage of the collaboration of chemists, physicist, and engineers to ensure both the production and the characterization of additives for asphalts by pyrolysis and the characterization of the improved asphalt performances from a rheological point of view.

3.1.1. Pyrolysis Approach as Waste Thermoconversion

The pyrolysis process allows for the conversion of a feedstock, mostly with a high carbon content (e.g., lignocellulosic biomasses, RDFs, plastics, tires), in three main products:

- a condensable fraction (bio-oil) rich in water, hydrocarbons, and oxygen-containing species [14,52–54];
- a mixture of gases (mainly CO, CO_2, and CH_4) that can be used, thanks to its heating value, to energetically sustain the process [14,52,55–58];
- a solid carbon-rich residue (char) [52,59].

The ranges of operating temperature, heating rate, atmosphere (the typology of inert gases), and residence time of the vapors and solids in the pyrolysis chamber can be adjusted based on the desired outputs, gathering the pyrolysis processes into four broad categories: slow, conventional, fast, and flash pyrolysis [52]. Heating rates vary from 0.1–1 °C/s (slow pyrolysis) to above 1000 °C/s (flash pyrolysis), while conventionally, the temperatures of the process lie between 300–600 °C.

To highlight the influence of the operating parameters on the product yields, in Figure 2, a comparison between the yields of the pyrolysis products derived from a ligno-cellulosic biomass obtained by tests performed at different final temperatures and different heating rates is reported. As a general indication, slow pyrolysis conditions are suitable for char production, especially at low temperatures, while for the same temperatures, fast or flash pyrolysis conditions are suitable for the maximization of gas and liquid productions.

In particular, at high temperature, if the process is conducted at a condition where the vapors residence time is prolonged (at a low heating rate, e.g., slow pyrolysis conditions), the yield of the gas fraction reaches a maximum, since secondary reactions (e.g., cracking) become relevant and the char evolves toward a structure with a reduced oxygen content (called primary char). Conversely, at a high heating rate (e.g., fast and flash pyrolysis conditions), the gas yield decreases to favor a higher production of the liquid fraction, since the secondary reactions (e.g., the decomposition into small molecules) are limited [52]. Further details regarding the pyrolysis of lignocellulosic biomass types can be found in the recent review by Giudicianni et al. [52], while details regarding the pyrolysis of MSW can be found in the review of Hasan [60].

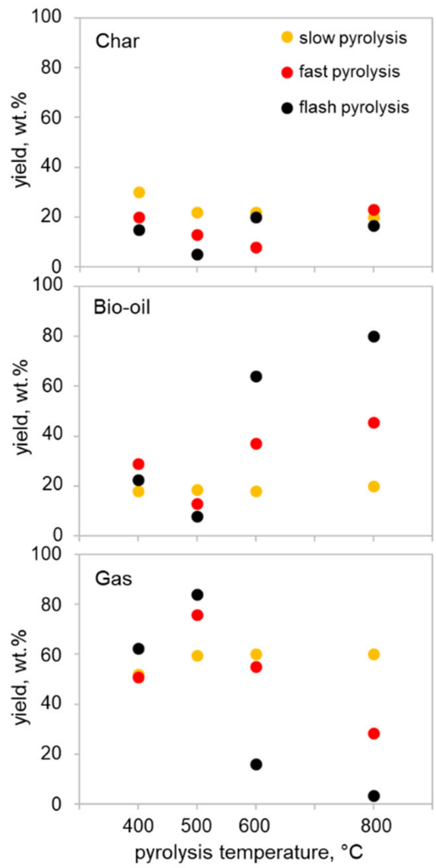

Figure 2. Product yields obtained from pine wood pyrolysis at different temperatures under slow, fast, and flash pyrolysis conditions (adapted from [52]).

Energy consumptions of the various types of processes are another important aspect to be taken into consideration for application purposes. However, to assess the economic performance of a given process, the whole productive chain, including the end-users of the pyrolysis products, should be taken into account. Life cycle assessment (LCA) becomes necessary in such an evaluation.

The pyrolysis process is a flexible thermoconversion strategy, since the composition of each pyrolysis product can be tuned by acting on suitable parameters. This optimization implies the detailed characterization of the composition of the starting feedstock, which is one of the major trending topics of this wide research area [52]. Standardized protocols (ASTM protocols) to define the elemental composition (C, H, N, S contents by ultimate analysis), the contents of moisture, ash, volatiles, and fixed carbon (by proximate analysis), and the heating value of a feedstock are conventionally adopted [61].

Regarding the ReScA project, the selected feedstocks (RDFs) are derived from urban waste management and stabilized according to the current legislation. RDF is the combustible fraction of MSW characterized by a high carbon content and a high calorific value, since its composition includes: hard plastics, packaging waste, textiles, wood, metals, and rubber [62]. RDF is produced in mechanical–biological plants for MSW sorting, as the final residue of the following sequential processes: (i) the recovery of recyclable materials (e.g., plastics, metals, glass, paper); (ii) the biological stabilization of biodegradable waste; (iii) the separation of inert waste [62].

RDF is characterized by a high compositional variability which influences its overall thermal behavior. The average RDF composition reported by different authors is the following: 15–35% plastics, 15–50% cellulosic paper and cardboard, 2–10% wood, 5–20% organics, and about 5–10% non-combustible matter [62–64].

The overall thermal degradation of RDF is mainly influenced by the thermal degradation of the two more abundant fractions (cellulosic and plastic fractions) [64]. RDF decomposes in a wider temperature range (200–600 °C, Figure 4), but at a lower temperature compared to carbon-rich materials [65]. Its low fixed-carbon, the highly volatile matter [64], and the presence of non-volatile matter between 10 and 20% (metals can catalyze decompositions) are responsible for such a pyrolytic behavior.

The depolymerization and monomer fragmentation processes of the RDF components regulate the relative quantities of solid (char), liquid (bio-oil), and gaseous fractions, especially those with lower molecular weights.

For a better understanding of the phenomena occurring in the thermal degradation of the RDF, and also to highlight how the heating rate and the final temperature can influence the latter, the mass loss (measured by thermogravimetric analysis, TGA) and the differential thermogravimetric signal (DTG) of a RDF, selected as a case study, are reported in Figure 3 for two different heating rates (5 and 50 °C/min). The mass loss as a function of the temperature or residence time is due to the concurrent phenomena of decomposition, oxidation, and loss of volatiles [66]. The differences observed for the two TG curves evidenced that the degradation mechanism is influenced by the heating rate and, as a consequence, that the relative amounts of the three fractions at the output of the pyrolysis process (gas, char, and bio-oil) can be tuned by operating on different parameters (mainly temperature range, heating rate, and gas residence time).

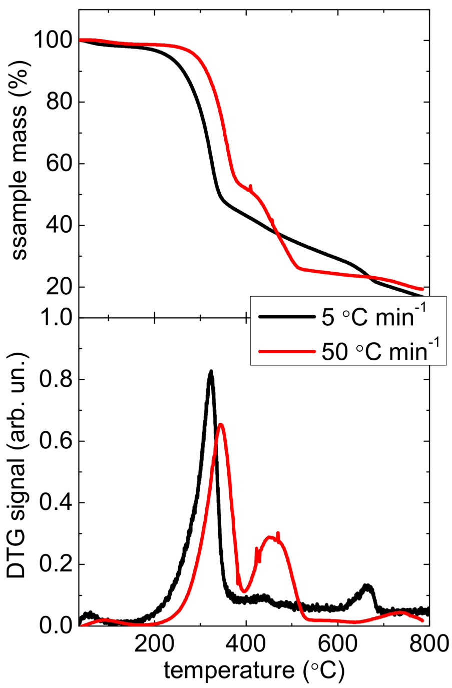

Figure 3. Mass loss (upper panel) and corresponding derivative curve of a RDF. Thermogravimetric analyses have been performed from 30 °C up to 800 °C on a Perkin–Elmer STA6000 under inert atmosphere (N_2, flux 40 mL/min), applying two different heating rates: 5 °C/min and 50 °C/min.

As a final remark, the superiority of the pyrolysis treatment of plastic wastes to obtain overall environmental performances better than those of conventional options, such as landfilling or incineration, has been proven by means of the LCA approach since 2005 [67]. More recently, Jeswani et al. [10] have carried out a deeper LCA analysis showing that, even if the pyrolysis treatment of mixed plastic waste has a 50% lower climate change impact and life cycle energy use than the energy recovery option, other impacts such as acidification, eutrophication, and photochemical and ozone formation, are higher than those for mechanical recycling and energy recovery due to the relatively high energy demand in the pyrolysis and purification processes. Therefore, the results of Jeswani et al. [10] underline the need to improve, in the future, the research effort to increase the carbon conversion efficiency of waste pyrolysis to further reduce its impact.

3.1.2. Asphalts Preparation, Aging, Rejuvenation Testing and Rheological Characterization

A wide array of standard rheological tests is usually employed to characterize the asphalt components (mainly bituminous fraction) and the asphalt prototypes.

Within the ReScA project, bitumen samples containing different amounts of char are prepared and the evaluation of their stability is achieved by different techniques: penetration grade experiments (EN 1426: 2015), ring and ball tests (EN 1427: 2015), NMR diffusion experiments, differential scanning calorimetry (DSC) measurements, rheometry measurements for G', G'', and tan delta, rutting and fatigue parameters, black diagrams analysis, microscopy imaging (optical, AFM), and infrared spectroscopy measurements. The char-modified bitumens exhibiting good stability are then used to prepare asphalt prototypes. The preparation of asphalt prototypes is carried out in accordance with standard protocols (UNI EN 12697-31) involving a gyratory compactor. In detail, the size distribution of the inorganic particles is chosen according to the Italian Standard Specifications [19], at the same time, meeting the limits imposed by the Superior Performing Asphalt Pavements method under the Strategic Highway Research Program (Superpave SHRP) [20]. Specific aggregate gradation for the asphalt specimen production are chosen to ensure anti-rutting phenomena [21] and following a mix-design method (UNI EN 933-1). Stability evaluation is achieved using the standard Marshall Stability Test (ASTM D6927).

To evaluate the anti-aging effects given by the char addition, aging tests are performed on char modified bitumens. The simulation of aging is carried out by the standard procedure of the rolling thin-film oven test (RTFOT) according to the standard protocol ASTM D2872-04, and the pressure aging vessel (PAV) test, according to the ASTM D6521 protocol. The characterization of the mechanical properties after the aging process is performed by the same analytical techniques used for the stability evaluations.

To test the effectiveness of bio-oil as a rejuvenator or as fluxing agent, aged bitumens samples are characterized by the aforementioned techniques and then treated with increasing amounts of bio-oil. The evaluation of the mechanical properties of the obtained samples and the comparison of such results with those of virgin and aged bitumens allow for the definition of the effect of the bio-oil addition.

The collection of all these characterization results is expected to strengthen the understanding of the mechanisms of interaction between bitumen constituents and additives in the form of nanoparticles responsible for the increase in performance and durability of the binder and the resulting asphalt.

As proof of the proposed approach, some preliminary results on a RDF, feedstock selected as a case study, are reported in the next section.

4. Preliminary Results: RDF as a Case Study

In this section, preliminary results on the characterization of bio-oil and char produced through RDF pyrolysis, selected as a case study, at different final temperatures, and their feasible use as rheological modifiers, rejuvenating agents, and antioxidant agents are reported.

The RDF used as the first feedstock for pyrolysis testing was provided by Calabra Maceri S.p.A. (Rende, CS, Italy).

The RDF was pyrolyzed in a tubular lab-scale quartz reactor under fast pyrolysis conditions (heating rate 30 °C/min) at three different final temperatures (550 °C, 650 °C, 750 °C). The final temperatures have been selected on the basis of the TG profiles reported in Figure 3.

Figure 4 highlights the chemical composition of bio-oils collected after each pyrolysis test. As it can be seen, the chemical composition of the bio-oil depends on the pyrolysis final temperature. It is interesting to note that the presence of specific compounds (for example, fluorene and 1-nonadecene) is scarcely influenced by the pyrolysis temperature, while other compounds (benzoic acid, for instance) are characterized by amounts that can vary as a consequence of a temperature change. This aspect is related to the occurrence of secondary reactions at high temperatures, leading to the decomposition of more reactive compounds [52].

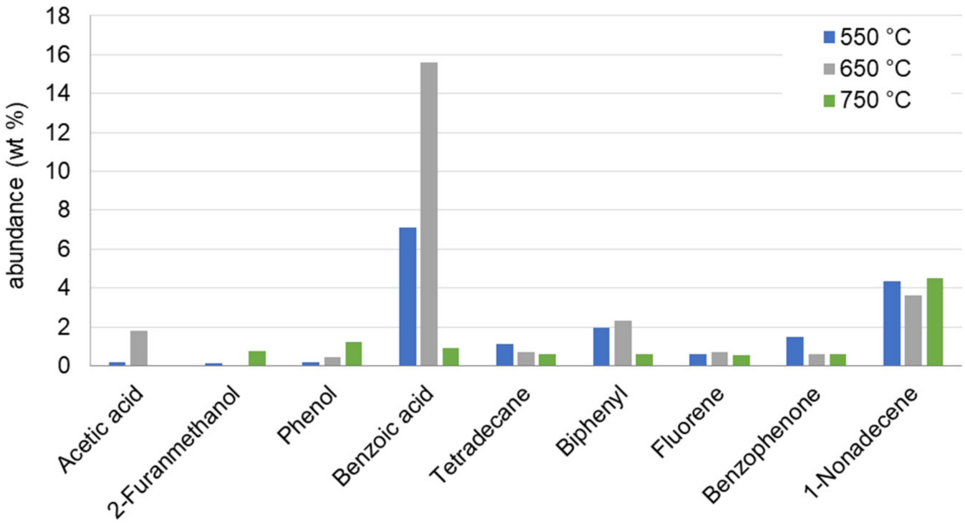

Figure 4. Relative abundance of selected species in bio-oils from RDF fast pyrolysis tests at 550 °C, 650 °C, and 750 °C. The abundances have been estimated by gas chromatographic analysis of acetone-diluted bio-oil solutions performed on an Agilent GC-MS instrument (7890 A/5972 C) equipped with an Agilent DB-624 capillary column.

When using the char as a bitumen filler in asphalt preparation, the relevant char features to take into account are: the composition, the surface chemistry, and the textural and morphological properties. These chemico-physical and morphological characteristics greatly affect the chemical interactions between the char particles (acting as a filler) and the macromolecules forming the bitumen. These influence the stability and/or the mechanical properties of the asphalt [27,68]. By acting on pyrolysis conditions, the possibility of influencing the chemical composition of the char can be achieved. For this reason, it becomes advisable to optimize the whole process by varying the pyrolysis conditions in such a way that the relative quantities of the desired pyrolysis products and their compositions match as much as possible those of the additives for asphalts.

Figure 5 evidences the influence of the final temperature on the chemical composition of char obtained from RDF fast pyrolysis. The results for the final temperatures of 550 °C, 650 °C, and 750 °C are reported.

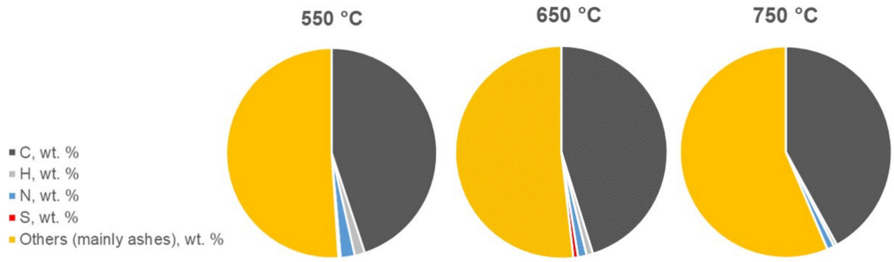

Figure 5. Compositional analysis of char samples derived from RDF fast pyrolysis tests at 550 °C, 650 °C, and 750 °C. C, H, and N contents were determined in accordance with the ASTM D3176 protocol by using a Leco 628 elemental analyser. S content was measured in accordance with the ASTM D4239 protocol by using a Leco 144 analyzer.

To demonstrate the feasibility of the usage of the liquid and solid products from pyrolysis tests as bitumen additives, bio-oil and char produced by the pyrolysis of a wood-based RDF supplied by Calabra Maceri S.p.A. (Rende, CS, Italy), have been tested at two different temperatures (550 °C and 750 °C):

- neat bio-oil (*P-Oil*) obtained from a pyrolysis test at 750 °C (temperature test allowing for the highest yield of liquid fraction);
- neat char, (*P-C1*) obtained from a pyrolysis test at 550 °C (temperature test allowing for the highest yield of solid fraction);
- a 50:50 *w*/*w* mixture of *P-Oil* and *P-C1* (*P-C2*).

The modified bitumen samples were prepared by adding 2 wt.% of the three additives to different aliquots of a neat bitumen. The bitumen used was a 50/70 penetration grade bitumen kindly supplied by Polyglass SpA (Ponte di Piave, TV, Veneto, Italy) and derived from a crude oil originating from Saudi Arabia, asphaltene content 32.4 wt.%.

Time cure tests to evaluate how the additive addition can change the mechanical properties of a given bitumen were performed. In particular, the effectiveness of their use as a rheological modifier, as a rejuvenating agent, and as antioxidant agents was evaluated. Rheology time cure tests were performed with a temperature ramp at a constant heating rate of 1 °C/min ($\tan \delta = G''/G'$) [69] under the regime of a small amplitude oscillatory shear at a frequency of 1Hz using a dynamic stress-controlled rheometer (SR5, Rheometric Scientific, Piscataway, NJ, USA) equipped with a parallel plate geometry (gap 2 mm, diameter 25 mm), and the temperature was controlled by a Peltier element (uncertainty ±0.1 °C). These conditions are those generally adopted for accurate studies on bitumen mechanical properties [70,71].

The time cure tests results are reported in Figure 6.

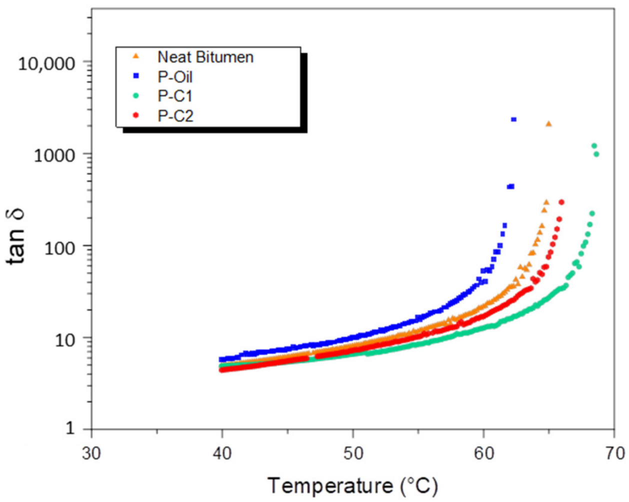

Figure 6. Results obtained from time cure tests on the three modified bitumens.

P-Oil is able to lower the transition temperature of the neat bitumen. This is an expected result because as far as it is known, only an oily compound has a softening ability, so bio-oil can be considered a bituminous fluxing agent. Conversely, *P-C1* and *P-C2*, showing a moderate modifying action, might be used as bituminous conglomerates fillers.

All the additive formulations were also tested as anti-aging agents. In Table 1, the transition temperatures of bitumens modified by *P-Oil*, *P-C1*, and *P-C2*, before and after the aging procedure, are reported.

Table 1. Transition temperature of bitumen samples modified by *P-Oil*, *P-C1*, and *P-C2* before and after aging.

Sample	Transition T (°C) ±0.1 before Aging	Transition T (°C) ±0.1 after Aging	Δ (°C)
Neat Bitumen	65.0	73.6	8.6
Bitumen + P-Oil	62.3	71.5	9.2
Bitumen + P-C1	68.5	75.5	7.0
Bitumen + P-C2	66.0	73.4	7.4

The rheological analysis showed that *P-Oil* is the only additive that can be used as a bituminous antioxidant. In fact, its tan δ tends to resist the hardening induced by oxidation.

The effect of pyrolysis-derived additives on the oxidized bitumen (aging simulated by the standard procedure of RTFOT, according to the standard protocol ASTM D2872) are shown by the mechanical spectra (results of time cure tests) reported in Figure 7.

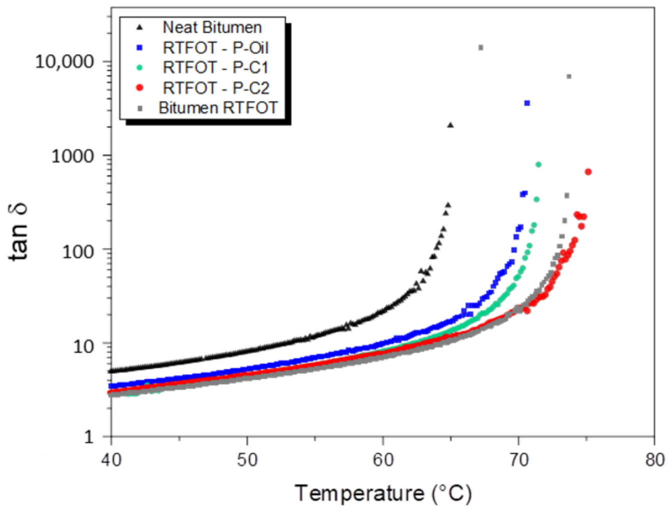

Figure 7. Time cure tests of neat bitumen, aged bitumen (bitumen RTFOT), and the three samples obtained by adding *P-Oil*, *P-C1*, and *P-C2* to aged bitumen.

As widely demonstrated in the literature, in order to understand the real regenerative capacity of an additive, it is necessary to make a preliminary rheological analysis. Since tan δ trend is similar to that for virgin bitumen, it is possible to claim that this additive might act as a rejuvenating agent [68].

According to the results in Figure 6, *P-Oil* and *P-C1* seemed to have the ability to rejuvenate the aged bitumen, since both showed an intermediate rheological behavior between the virgin and aged samples. On the other hand, *P-C2* had a profile almost similar to that of the aged bitumen, so the possibility of using it as a bituminous regenerator is excluded.

These preliminary tests demonstrated that the pyrolysis products act in different ways when integrated in the formulation of a bitumen, and they can also effectively act as rejuvenating agents.

This work is expected to have important impacts, in both technological and social fields, with beneficial effects on the economy, as detailed in the next section.

5. Expected Impacts in Technological, Social, and Economic Fields

The approach proposed by the ReScA project is expected to impact the quality of people's lives, fostering technological, economic, and social development.

The focus on the pyrolysis process foresees related advantages: the production of energy vectors, smaller dimensions of treatment plants and their cleaning sections, with consequent lower investment costs, and in general, greater global efficiencies, as well as operating flexibility and reduced greenhouse gas emissions.

In the vision of the ReScA project, RDF is not used to produce energy ("quaternary recovery", according to the European waste hierarchy introduced by the waste directive (Dir. 2008/98/EC) and recently amended in the Circular Economy Package of 4/7/2018), but as a starting point for added-value materials recovery ("tertiary recovery") to be used for the production of asphalts.

From the technological point of view, the use of char to enhance bitumen is a promising strategy to exploit the use of carbonaceous nanoparticles as modifiers since, at the present, their application, in spite of the advantageous results achieved on fullerenes, nanotubes, and graphene related materials [25,26], is limited due to the high production costs. The availability of carbonaceous particles at a low cost and with high performance as bitumen enhancers will explode studies in this sector. It has been predicted that the bitumen modified with char will have a greater resistance to cracking and rutting phenomena occurring at both high and low temperatures. This greater resistance to thermal fluctuations would undoubtedly offer greater safety for motorists and a drastic reduction in road maintenance activities. Moreover, it can be stated that the use of char as a modifier for asphalt, in addition to giving better mechanical performance and an increase in shelf-life, can also lead to significant advantages in the regeneration phase. Indeed, the use of bio-oil for the regenerative purposes for an aged asphalt could reasonably be effective in establishing synergistic effects with the char already present in the improved asphalt. The hydrocarbon molecules present as a fraction of the bio-oil are chemically similar to the carbonaceous particles of char, offering an enhanced rejuvenating effect, thanks to adsorption and chemical interaction phenomena. This would represent a breakthrough in the use of multi-functional and multi-effect additives, providing safer, longer-lasting, easy-to-regenerate roads with reduced maintenance and production costs. A study conducted in 2008 [72] estimated that the energy consumption reduction would be about 23% if an asphalt was reused for the construction of new road pavements. This result is in accordance with those obtained by a project financed by the European Community [73] and highlights the environmental advantages of the reuse of exhaust asphalts (a lower release of heavy metals and polycyclic aromatic hydrocarbons (PAHs)).

The recent work of Moins et al. [19] indeed, demonstrated through LCA studies that with respect to the total economic and environmental impact of asphalt industry:

- the bitumen production is the main hotspot and accounts for 12% to 41% of the environmental impact and 10% to 39% of the economic impact;
- the virgin aggregates supply has an economic impact from 5% to 16%;
- the transport of raw materials contributes between 10% and 24% to the environmental impact and between 6% to 14% to the economic impact;
- plant operation activities have an economic impact from 12% to 24%;
- the energy use in asphalt mixture production has an environmental impact ranging between 11% and 24%.

The approach suggested by ReScA pointed towards a reduction in the consumption of bitumen for the production of any new asphalts and would boost the strategies for the regeneration of aged asphalts, thus limiting exhaust asphalt landfilling and new asphalt production. All this, therefore, would lead to a reduced and rationalized use of petroleum materials and derivatives, as well as aggregates and sands, constituent elements of asphalts extracted from natural resources, achieving economic returns, resource preservation, and landscape and environmental protection.

6. Conclusions and Future Perspectives

The simultaneous coupling and closing of waste pyrolysis and asphalt cycles has been proposed. In this approach, the solid (char) and liquid (bio-oil) residues of waste pyrolysis can be used as added-value ingredients to (i) produce improved asphalts, with increased performances for motorists' safety and with an increased life-cycle, and (ii) regenerate exhaust asphalt. In this way a virtuous mechanism where urban wastes are no longer disposed to landfills has been individuated. In addition, the asphalt prolonged life-cycle and the possibility to regenerate asphalt by pyrolysis-derived oil will reduce wastes, slowing down landfilling. Of course, the pyrolysis conditions (temperature, temperature ramp, duration of thermal treatment) are all factors that can be tuned to optimize the pyrolysis process to obtain residues with ad-hoc characteristics for asphalt technology. The benefit of this approach is also to be seen in a circular economy perspective. Sustainable development is pursued through research and innovation and through the improvement of infrastructures. To increase the knowledge on process development, scientists, policymakers, and entrepreneurs must work together to develop new and innovative approaches to waste re-use that address both safety and sustainability.

The overall perspective of the ReScA project is to contribute to the recovery of added value materials through the valorisation of wastes and their exploitation as additives for improved bitumens and asphalt production. The main goal of the ReScA project is to pursue both process sustainability and environment protection by taking these into account for all levels of the production cycle, namely from the limitation of waste disposal in the environment to the development of new protocols for bitumens and asphalt production and management.

The choice of pyrolysis, an extremely promising and flexible thermochemical conversion technology (but not yet consolidated on a global scale) will allow the verification of its potential and applicability in terms of sustainability and in the framework of the circular economy paradigm.

The proposed idea integrates the urban waste transformation process with that of asphalt production, leading to:

- the promotion of cleaner technologies for the use of urban wastes;
- the production of road materials with improved properties from the reuse of urban wastes;
- an alternative applications of pyrolysis products (liquids and solids) outside of the fuel and chemicals industries;
- the reduction of the costs for the construction of safer and longer-lasting road pavements and those related to maintenance activities;
- the integration of systems and processes;
- the optimization of low-cost processes by operating on the parameters involved;
- energy saving and environmental protection (LCA analysis indicates that the chemical recycling of plastic wastes through pyrolysis has a climate change impact 42% lower than the energy recovery option) [10].

These aspects are in accordance with the community policies dealing with the circular economy approach, the Sustainable Development Goals pillars, and the Kyoto Protocol, since they pursue the security of energy supply, a sustainable use of urban solid wastes, the reduction of gaseous emissions, landscape and environmental protection, and the limited consumption of resources. The recovery and reuse of wastes are strongly encouraged, since wastes are considered as a source of new functional materials.

The use of char to enhance bitumen properties, exploiting the char composition and characteristics that are very close to those of the carbonaceous nanoparticles currently used for this purpose (fullerenes, nanotubes, and graphenes) [26], is a very promising strategy, first of all, because a fine modulation of char morphological and functional characteristics (granulometry and porosity, to name a few) can be obtained by operating on the pyrolysis process parameters. These interesting potentials would make char an excellent candidate to replace fullerenes, nanotubes, and graphenes, which, despite being recently considered as very valid additives for bitumen due to their high performance-enhancing abilities [26], currently have a very limited application due to their high production costs [25].

To conclude, one aspect of complex systems physics has to be considered: it is known that often, different additives yield an overall effect that is not the sum of the two single effects, but the result of synergistic effects [74]. Therefore, the simultaneous use of char and bio-oil can enlarge the scenario of beneficial effects in bitumens. For these reasons, the ReScA project will foster future developments in the use of multi-functional and multi-effect additives, a quite novel field in bitumen and asphalt technology. The benefits achievable through safer, longer-lasting roads, with reduced maintenance and production costs, and with an overall reduction of wastes to be disposed into landfills, would be indisputable.

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