The Role of Solvent and Catalysts on Co-Liquefaction of Coal and Waste

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It is predictable that liquid fuels will be needed for long distance transport sector for quite some years. Thus, it is imperative to find alternative fuels to reduce the dependency on petroleum derived fuels and to decrease the negative environmental impact. Co-liquefaction of coal and wastes, like plastics, to produce liquid fuels and raw materials for several industries may play an important role in the near future, because it will decrease the problems associated with the dependency of only one raw material and also it will allow taking profit of the suitable properties of each one, while diluting the disadvantageous characteristics of coal. The use of plastics, namely polyethylene (PE) favoured coal liquefaction, as PE macromolecules are easier to break down and to form smaller liquid molecules than coal. To improve the production of liquid compounds by coal liquefaction solvents with different hydrogen donor capabilities were tested, such as: methylnaphthalene and tetralin. Tetralin led to the highest liquid yields and conversion, due to its hydrogen donor capacity. Some commercial available catalysts, like FCC (Fluid Catalytic Cracking) and Co-Mo based were also tried. Coal impregnated with some metals like iron (Fe) and molybdenum (Mo) was also tested. Impregnated coal, especially with Mo showed to have a better performance than the commercial catalysts. Liquid yield obtained during co-liquefaction of coal and PE when coal was impregnated with Mo was around 66 wt%. The use of tetralin allowed increasing this value around 44 %.

1. Introduction

The need of finding alternative fuels, associated with the decrease of petroleum reserves, has led to the increasing interest of using direct coal liquefaction (DCL) to produce liquid fuels, as coal reserves are bigger than petroleum ones. On the other hand, coal may present high contents of sulphur, nitrogen, chlorine and heavy metals, which brings new challenges to the use of this fossil fuel. Co-liquefaction of coal and wastes especially plastics, may help to control coal negative environmental bearing (Li et al., 2016) and help coal liquefaction, as plastics are easier to liquefy, they may favour mass and energy transfer (Pinto et al., 2013).
Coal macromolecules are broken down during DCL, hence the radicals formed need hydrogen to be stabilized and form smaller molecular structures, which originate gases and liquids products at room temperature. Solids are also formed, they are mainly composed by coal inorganic matter and by elemental carbon, due to the thermal decomposition of unconverted organic compounds. DCL needs severe conditions up to 30 MPa of hydrogen pressure and temperatures between 400 and 500 ºC. Specific catalysts (Trautmann and Traa, 2013) and the presence of hydrogen donor solvents (Barraza et al., 2016) may also promote the formation of liquid compounds. There is much information about coal liquefaction. Shan et al. (2015) reported information about the Shenhua Shendong bituminous coal continuous facility. Niu et al. (2016) studied interactions between hydrogen-donor and non-donor solvents in direct coal liquefaction. However, published data about co-liquefaction of coal and plastics are scarce. Most of the co-liquefaction studies were published in the late 1990s beginning of 2000.

Domínguez et al. (2001) tested two plastic wastes (LDPE-low density polyethylene and HDPE-high density polyethylene) mixed with a high-volatile bituminous coal in different blends at temperatures between 400 and 500 ºC and found that coal could act as a hydrogen radical source for the stabilisation of the alkyl free radicals formed from the polyalkenes. Also, Wang and Chen (2002) studied the catalytic co-liquefaction of coal with LDPE using an iron-based catalyst. The catalysts used were sulphur promoted iron oxides, ferrous sulphide, ferrous sulphate and mineral pyrite and the tests were performed in an autoclave at 10 MPa hydrogen pressure, 450 ºC and 60 min of reaction time. This study showed that the presence of sulphur in the catalyst improved the total conversion and oil yield.

The main research challenge is to achieve high liquids yields and to improve the viability and environmental performance of DCL. Thus, coal was co-liquefied with plastics wastes and the effect of different types of catalysts and solvents on promoting the production of liquids by co-liquefaction was studied. The performance of tetralin that is a solvent with high hydrogen donor capability was compared to that of methylnaphthalene that is a non-hydrogen donor solvent. The coal used in the co-liquefaction tests was previously impregnated with 1 wt% of Fe or with 1 wt% of Mo and the liquids yields and coal conversion were compared with the values obtained without coal impregnation. Two commercial catalysts FCC (Fluid Catalytic Cracking) and Co-Mo, commonly used in petroleum refineries were also tested as heterogeneous catalysts.

2. Experimental Part

Coal liquefaction and co-liquefaction tests of coal blended with PE were done in a batch reactor, an autoclave made in Hasteloy C276 by Parr Instruments. The reactor was first loaded with coal or a mixture of brown coal with 50 wt%. of PE wastes. This mixture is a good option, as considerable liquid yields were obtained, because PE is easy to liquefy (Pinto et al., 2013), while using significant coal content. Brown coal (BC) came from the Czechoslovak Army Mine (CSA) that is an opencast brown coal mine located in the North Bohemian Basin of the Czech Republic. In Table 1 are shown the proximate and ultimate analysis of the materials used.

Table 1: Proximate and ultimate analysis of the feedstocks used in co-liquefaction.

	Proximate analysis (ar wt%)				Ultimate analysis (daf wt%)				
	M	Ash	V	FC[b]	C	H	N	S[a]	O[b]
Coal	6.1	3.9	50.1	39.9	74.7	7.0	1.2	1.0	16.1
PE	0.0	0.1	99.8	0.1	85.7	14.3	0	0	0

M: moisture; A: ash content; V: volatile matter; FC: fixed carbon; ar: as received basis; daf: dry and ash-free basis.
[a] Total S. [b] By difference.

The effect of two solvents on products yields was studied. Tetralin was used as a hydrogen donor solvent and methylnaphthalene was used as a non-hydrogen donor solvent. A feedstock/solvent ratio of 2.5 wt. was used.

Two commercial catalysts FCC (Fluid Catalytic Cracking) from BASF and Co-Mo were used as heterogeneous catalysts. FCC is widely used in petroleum refineries to convert the high-boiling, high-molecular weight hydrocarbon fractions of petroleum crude oils into more valuable gasoline, olefinic gases and other products. The Co-Mo is also used in petroleum refineries. CoMo and FCC are commercial catalyst and thus there is not much information available about them. For commercial catalysts a coal/catalysts ratio of 1 was used. Furthermore, brown coal impregnated with Fe (Fe (1 wt%)/BC) or with Mo (Mo (1 wt%)/BC) was also tested. These impregnations were carried out by Soluciones Cataliticas Ibercat SL.

The autoclave was purged with nitrogen and pressurised to 3.45 MPa of hydrogen. Then, it was heated and kept at 420 ºC during 60 min. These experimental parameters were selected according to preliminary tests. Next, the autoclave was cooled down to room temperature and gases were measured, collected and analysed by gas chromatography (GC) to determine the contents of CO, CO_2, H_2, CH_4 and other gaseous hydrocarbons, referred as C_nH_m, including alkanes and alkenes with carbon atoms from C_2 to C_4. Solid and liquid products were weighted.

The liquid products directly collected from the autoclave were distilled according to ASTM D86 to obtain three fractions: the lighter one with a distillation temperature below 150 ºC, the second fraction distilled in the range from 150 ºC to 270 ºC and the residual fraction had a distillation temperature beyond 270 ºC. The first two distillates were analysed by GC and GC/MS. Solids were extracted in a Soxhlet extractor, sequentially with n-hexane, toluene and tetrahydrofuran (THF) to determine the amount of liquids impregnated in solids. Total liquids yields were calculated considering the sum of the liquids directly retrieved from the autoclave and the liquids extracted from the solid product.

At least two sets of runs were repeated at the same experimental conditions, to assure the reproducibility of experimental results to be below 5 %.

3. Results and discussion

3.1 Effect of solvent type on products yields and conversion

Figure 1 (a) presents the yields of liquids retrieved from the autoclave (direct liquids) plus the liquids extracted from the solid product (total liquids), using *n*-hexane, toluene and tetrahydrofuran. The water produced in each trial arose from the coal moisture and to reactions that release water (decarbonylation and hydrodeoxygenation, for example) and it was not included in the liquid yields. Thus, results are presented on % of dry and ash free coal.

When no solvent was used, the lowest liquid yields and the lowest conversions were obtained, Figure 1 (a). Co-liquefaction of coal blended with 50 wt% of PE allowed increasing both liquid yields and conversion, about 55 and 52 %, respectively, while the number of solids was observed to decrease around 42 %. As PE is easier to liquefy than coal, the presence of PE might have favour mass and energy transfer and thus coal liquefaction. The presence of solvent during coal and PE co-liquefaction increased further liquid yields and conversion.

As shown in Figure 1 (a), the highest liquid yields, the highest conversions and the lowest solid yields were obtained in presence of tetralin, which is in agreement with the high hydrogen donor capability of this solvent.

The use of tetralin in co-liquefaction of coal mixed with PE led to an increase in liquid yield of around 77 %, while conversion rose about 88 % in relation to the absence of solvent. Methylnaphthalene led to liquid yields and conversions higher than those obtained without solvent, but lower than those with tetralin. On the contrary, solid yields were higher than that with tetralin, but lower than the values obtained without solvent. Gas composition obtained by coal liquefaction and co-liquefaction of coal and PE is presented in Figure 1 (b). For all experiments, alkanes contents were higher than those of alkenes and gaseous hydrocarbons content decreased with the rise of carbon atom. Thus, besides methane, ethane was the gaseous hydrocarbon with the highest content. CH_4 content was higher than C_nH_m for most situations with CH_4/C_nH_m ratios usually higher than 2. CO content was very small for all tests. Instead of H_2 content, Figure 1 (b) presents H_2 consumption.

Hydrogen consumption was lower for co-liquefaction of coal and PE than for coal liquefaction, due to the presence of PE that may have contributed to the enrichment of the reaction medium with hydrogen. Tetralin led to the lowest hydrogen consumption, due to its high capability to supply hydrogen to the reaction medium. Hydrogen consumption with methylnaphthalene is similar to that without solvent, because this solvent does not supply hydrogen. Hydrogen consumption was the lowest with tetralin, thus there was more hydrogen in the gases and the contents of all other gaseous compounds were lower. The results shown in Figure 1 (a) agree with those of Figure 1 (b), as the solvent with the highest hydrogen-donor capability (tetralin) led to the lowest hydrogen consumption.
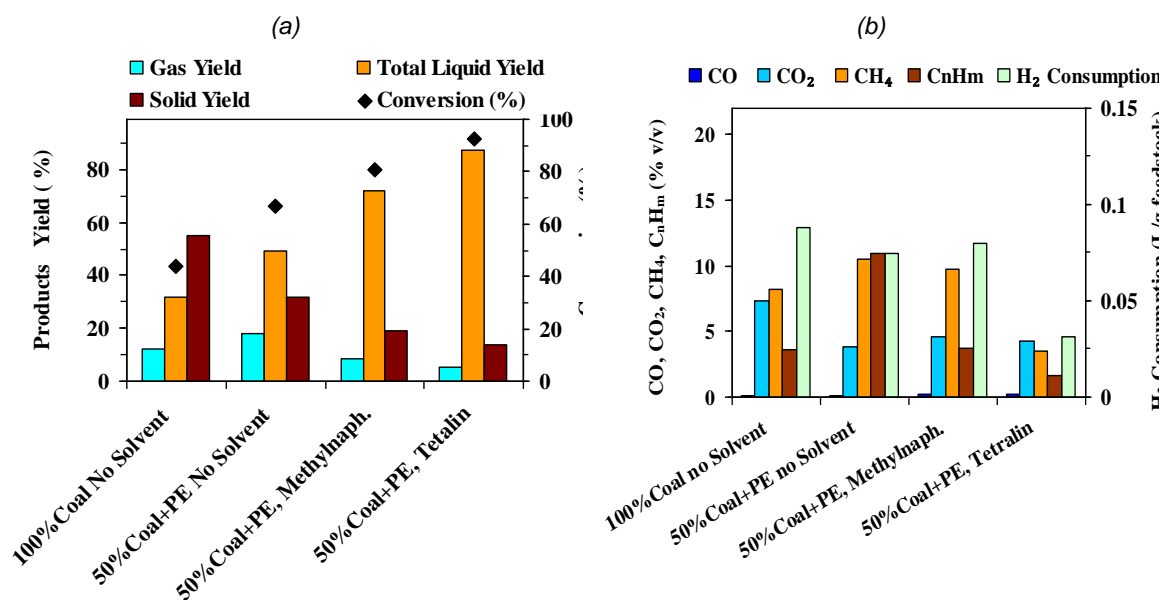

Figure 1: Comparison of coal liquefaction with co-liquefaction of coal and PE wastes with different solvents. Other experimental conditions: 420 ºC, 60 min, 3.45 MPa (initial H_2 pressure). (a) Products yields and conversion. (b) Gaseous products composition.

3.2 Effect of catalyst type on products yields and conversion

In Figure 2 may be analysed the effect of catalyst on co-liquefaction of coal with 50 wt% of PE wastes. The results obtained without solvent may be compared with those obtained in presence of tetralin.
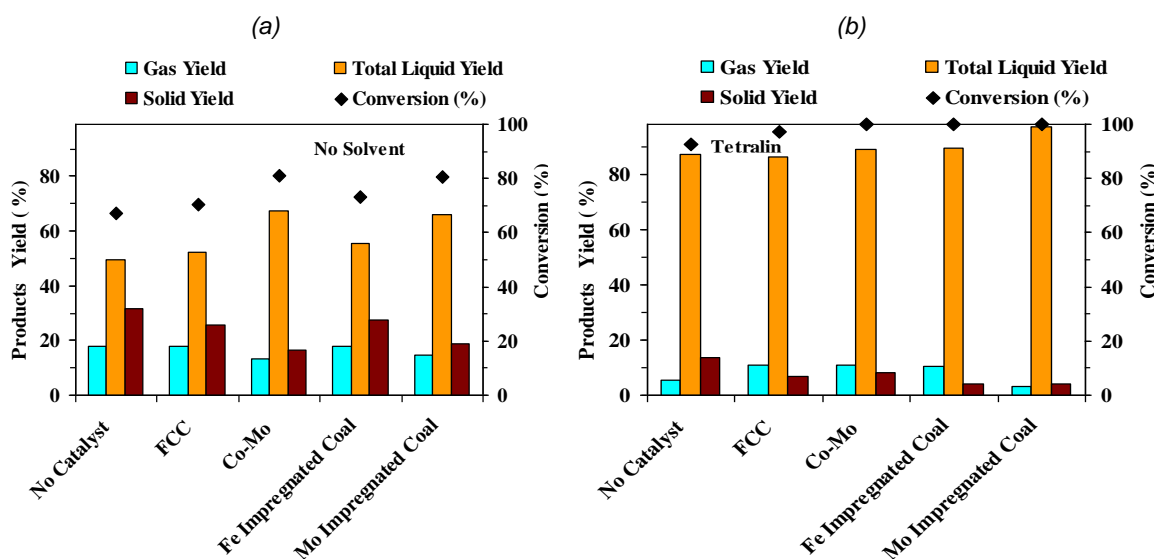

Figure 2: Effect of catalyst on products yields and conversion obtained for co-liquefaction of coal with 50 wt% of PE wastes. Results are presented on % of dry and ash free coal. Other experimental conditions: 420 ºC, 60 min, 3.45 MPa (initial H_2 pressure). (a) Without solvent (b) In presence of tetralin.

Figure 2 (a) shows that without solvent, the presence of catalyst favoured coal and PE co-liquefaction. The highest liquid yields and conversions were obtained with Co-Mo and with coal impregnated with Mo. The values obtained for products yields and conversions were quite similar, as the differences are within the experimental error. These values were higher than those obtained with Fe impregnated coal, whose performance was better than that obtained in presence of FCC. Without catalyst the lowest liquid yields and conversions and the highest amount of solids were obtained.
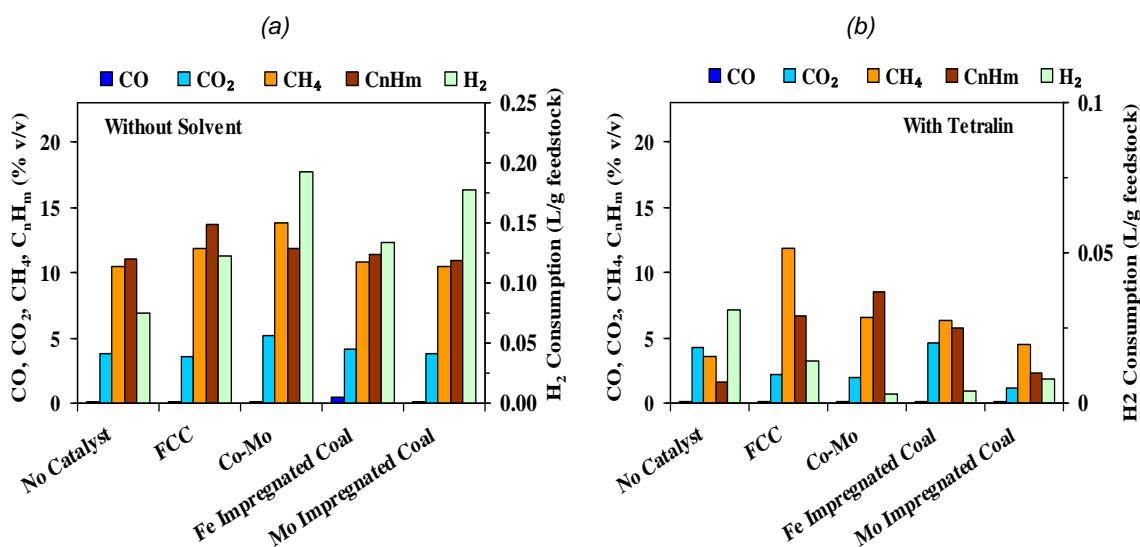

Figure 3: Effect of catalyst on gaseous products composition. Other experimental conditions: 420 ºC, 60 min, 3.45 MPa (initial H_2 pressure). (a) Without solvent (b) In presence of tetralin.

In presence of tetralin, Figure 2 (b), the use of catalyst is also beneficial, though the increase in liquid yields and conversions are much smaller, because of tetralin hydrogen supply during co-liquefaction. With tetralin the best performance was obtained with Mo impregnated coal, as the highest liquid yield and the lowest gases and solid yields were obtained. The results obtained with Fe impregnated coal are similar to those obtained with Co-Mo catalyst. The results obtained with FCC were only slightly better than those in absence of catalyst.

In Figure 3 (a) may be observed that in absence of solvent, the use of Co-Mo led to the highest hydrogen consumption, which was slightly higher than the value obtained when Mo impregnated coal was used. Hydrogen consumption in presence of FCC was lower than that obtained when Fe impregnated coal was tested. In general hydrogen consumptions presented in Figure 3 (a) are in agreement with Figure 2 (a) values, as higher consumptions correspond to higher liquid yields and conversions. As expected hydrogen consumption in presence of tetralin, Figure 3 (b) was lower than the values obtained without solvent, due to tetralin capacity to donor hydrogen to reaction medium. Hydrogen consumption in presence of Co-Mo was similar to that obtained with Fe impregnated coal, which agrees with the similar liquid yields and conversion. These consumptions were lower than that obtained with Mo impregnated coal, probably because with the later catalyst, higher liquid yields and conversion were attained. The highest hydrogen consumption corresponds to the situation when no catalyst was used, which corresponds to the lowest liquid yields and conversion.

Gaseous hydrocarbons content decreased with the rise of carbon atom, thus CH_4 content was higher than that of C_2H_6 and C_4 compounds showed the lowest contents. Gaseous alkanes contents were always higher than the corresponding alkenes, hence C_2H_6 concentration was higher than that of C_2H_4. In presence of tetralin hydrocarbons contents were lower than when no solvent was used, because hydrogen consumption was the lowest with tetralin, thus there was more hydrogen in the gases and the contents of all other gaseous compounds were lower. In generally CH_4 and C_nH_m contents were similar, being CH_4/C_nH_m ratios usually around 1 when no solvent was used and no higher than 2 in presence of tetralin. CO content was very small for all tests.

Products liquids analyses showed that during liquefaction, part of tetralin was converted into naphthalene, as shown in Figure 4, which agrees with the hydrogen donor capability of this solvent, as 4 hydrogen atoms are supplied to the reaction medium when tetralin is transformed into naphthalene. It was also checked the presence of other compounds that might have been formed by tetralin decomposition. Decalin was detected, but in lower content than naphthalene. When methylnaphthalene was used as solvent, it was detected that some of this solvent was converted into naphthalene, probably due to cracking reactions. When coal and PE were used as feedstock tetralin decomposition into naphthalene was lower, probably because PE liquefaction supplied some hydrogen to reaction medium.
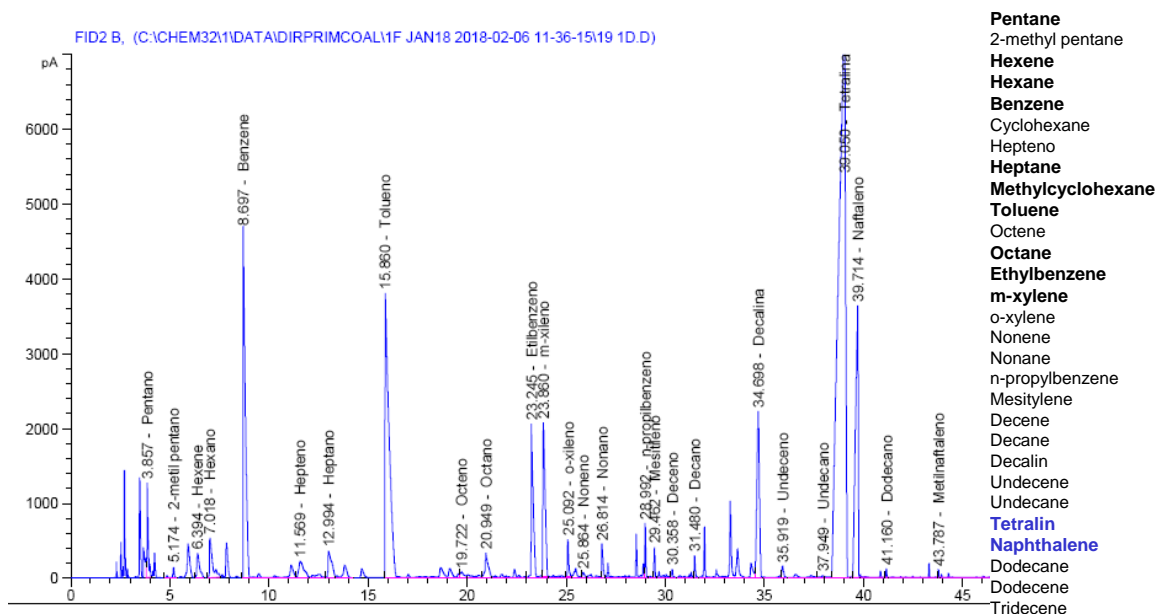

Figure 4: GC Analysis of lighter liquids obtained by co-liquefaction of 50:50 blend of coal and PE with tetralin.

The determination of liquids composition is a difficult issue, due to the huge number of compounds formed, most of them in small contents, as shown in Figure 4. This task is even more difficult in presence of solvents, because the liquid compounds formed are much diluted. Figure 4 shows a list of the compounds detected in the lighter fractions to illustrate the analysis that have been done. The compounds detected with the highest contents are

presented in bold and solvents are in blue colour. Liquids composition depended on the type of solvent and catalyst used, however, in general the dominant compounds were n-alkanes, branched alkanes were found with much smaller concentrations. Besides, the presence of toluene, benzene and xylenes, extended series of alkylbenzenes, including trimethylbenzenes were also identified. Naphthalene, methyl, dimethyl, and trimethylnaphthalenes were present in heavier fractions, but in lower concentrations than the alkylbenzenes. Small contents of alkylphenanthrenes were also identified, it is possible that these aromatic species have been derived predominately from the coal. Liquids complete analysis is still in progress, due to the complexity of liquids analyses, as several liquid fractions have to be analysed (3 distillation fractions plus 3 more fractions from solids solvent extraction with hexane, toluene and THF), many compounds are present in each fraction and most of them in small concentrations.

4. Conclusions

The presence of PE wastes seems to be beneficial for coal liquefaction, as it increased liquid yields and conversions, around 55 and 52 %, respectively. As co-liquefaction mass and energy transfer were facilitated by PE wastes, the amount of H-donor solvents may be decreased.

The use of tetralin improved co-liquefaction process, as its conversion into naphthalene allowed supplying hydrogen to the reaction medium, thus liquid yield was observed to increase around 77 %. In presence of tetralin, molecular hydrogen consumption was lower than that obtained with no added solvent, thus lower hydrogen pressures may be used.

Coal impregnated with Fe or Mo showed to be a suitable option to promote coal liquefaction, especially with Mo, as liquids yields and conversions increased.

Acknowledgments

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