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Review Article

Fischer-Tropsch Hydrocarbons as Processing Aides in Injection Molding

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ABSTRACT

Polymer producers and converters are continuously evaluating options to reduce costs by producing faster, reducing energy consumption, reducing scrap and improving finished article mechanical and aesthetic properties. Recently, however, sustainability and overall environmental impact have also become prominent themes for converters.

Processing aides are commonly used in blown film extrusion and injection molding. Specifically in injection molding silicone spray, fluoropolymers and oleochemicals are used. An alternative is to use higher molecular weight Fischer-Tropsch (FT) hydrocarbons as a polymer processing aide and mold release agent due to its good compatibility with the polymer compound matrix. Formulating with these hydrocarbons allows the converter to reduce cycle time, produce faster to reduce labor, to reduce energy consumption and improve certain properties of the injection molded article. Ultimately FT as a polymer processing aide could be an important tool to a converter to reduce manufacturing costs and improve quality.

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Introduction

The plastics industry has contributed significantly to the world economy and is seen as essential in several durable and nondurable applications. Plastics have replaced several materials in numerous applications, and mostly provide a good combination of physical properties and cost. Injection molding is a significant part of the polymer conversion industry. Worldwide, the market was over \$225 billion in 2016 [1]. It is thought that the global injection molding market may reach \$340 billion in 2024 [2]. The main growth area appears to be the automotive sector. The electronics industry is also a rapidly growing segment [2].

Although plastic injection molding has undergone significant improvements over more than 70 years, there are still continuous efforts to minimize production costs. Cycle time improvement and reduction of the scrap rate can have a significant influence on the profitability of an injection molder. The lifetime of a typical injection molding machine is expected to be around 10 to 15 years [3]. While equipment is not frequently replaced, the replacement costs is generally high and a fast return on the investment can provide a competitive advantage. Similarly, many injection molding customers are looking at efficiency improvements that could be implemented without significant capital spend. Additives are, therefore, attractive as they can be implemented with relative ease and relatively low cost. The paper will discuss the role of processing aides and then focus on the use of Fischer-Tropsch molecules as processing aides in the polyolefin injection molding process.

Processing Aides for Injection Molding

It is possible to distinguish between two types of additives that could improve efficiency during injection molding: processing aides and mold release agents. Mold release agents in polyolefin processing are typically silicones. However, in this section the focus will be on processing aides and their potential benefits during polyolefin injection molding.

Oleochemicals (including metal stearates), fluoropolymers, low molecular weight waxes and certain other oleochemicals can be used as processing aides in injection molding. Additives like glycerol monostearate, ethylene bis stearamide, alcohol ethoxylates and erucamide have been used in injection molding to improve processing [4]. Typically, these additives are added at low levels (< 0.2%). Increasing the concentration to the levels required to act as a processing aid (> 0.5%), could have negative effects on downstream processing like printing and accumulation in water. Fluoropolymers are effective but expensive and also under increased environmental scrutiny [5]. Metal stearates and oleochemicals can, however, result in screw slip and deposit build-up, create organoleptic issues, degrade forming color issues, which are undesirable effects.

The oldest and most subtle form of process aide is the low molecular weight component of a polymer's molecular weight distribution. These short chain molecules typically improve flow, while, if added at low concentrations, do not result in a significant deterioration in the mechanical properties [4]. However, polyolefin resin production purposely eliminates low molecular weight fractions before addition of stabilization additives. These low molecular weight fractions can be added directly into the polymer and result in an improvement in the melt flow rate.

Fischer-Tropsch (FT) processing aides are structurally similar to the low molecular weight part of a polyethylene molecular weight distribution. Fischer-Tropsch process aides are also highly compatible with polypropylene and other polyolefins. FT have been used as processing aides in injection molding for more than 15 years [4]. Given the properties of these molecules, they are fully compatible with PP and PE resins, potentially eliminating some of the issues that could be experienced with the use of external materials like silicone or internal process aides like oleochemicals.

Fischer-Tropsch Processing Aides

Fischer-Tropsch Processing Aides (FTPA) are produced by the Fischer-Tropsch synthesis process [4]. The FT process converts coal or natural gas into hydrocarbon products. This process is well known for the production of fuels (diesel, gasoline) and also chemicals, and has been commercially used in South Africa since 1950 [6]. The first commercial wax from this process was introduced into the market in 1955.

During the first step of the process, natural gas is desulphurized and then fed into the reformer unit. This unit produces synthesis gas (syngas), consisting of hydrogen and carbon monoxide. Syngas is then converted in the process to on-purpose hydrocarbons. The hydrocarbons can be simply classified into a wide range of cuts yielding, paraffin, medium and high melting waxes. Properties such as the crystallinity, melting point, congealing point, needle penetration, and molecular weight distribution define the product outputs of the Fischer-Tropsch distillation process. These molecules can then be further hydrogenated or functionalized by oxidation, saponification, maleation, or addition of other functional groups.

The high-melt point FT Processing Aides have been used extensively in polymer processing, including injection molding, PVC processing, masterbatch manufacturing and polyolefin extrusion [4,7-10]. Unlike thermally degraded waxes and byproduct PE waxes (BPPE), FT molecules are on-purpose produced and can be manufactured to very tight specifications, controlling very precise carbon chain distributions.

Table 1 shows the typical properties of the FTPA, used in this study. This FTPA has been in the market for more than 15 years, where the benefits have been shown in a variety of applications.

 Table 1: Typical properties of FT Processing Aides commonly

 used for Injection Molding in comparison with PE waxes

Properties	Fischer Tropsch Processing Aide	PE waxes				
Drop melting point (°C)	115	101~106				
Viscosity at 135 °C (cPs)	<10	>200				
Molecular structure	Mostly linear	Branched				
Molecular weight	600-1200	2000~12000				

FTPA are typically significantly lower in molecular weight and viscosity compared to conventional PE waxes.

Although a comprehensive mechanism of the working of FTPA in this application has not been completely corroborated, it is typically deemed to show benefits by proceeding along the subsequent scheme: FTPA are fully soluble in the polymer matrix (being non-polar). Due to this compatibility and its mostly linear structure, it penetrates the polymer matrix and fill the free void volume. These FTPA allow the longer molecules to move more easily past or over each other, thereby lowering the viscosity (improved flow properties) of the mixture. This easier movement enables ease of processing, improved productivity and efficiency. In filled systems, the low surface energy assists In pigment/filler coating, thereby facilitating dispersion. These molecules have been shown to be effective in both low and high MFI polyolefins [4]. Potentially, these processing aides could enable the use of lower MFI polymers, with the added benefit of better physical properties. These processing aides are effective in both unfilled and filled formulations.

Laboratory Studies: The Effect of FT Processing Aides on PP Injection Molding

In the current study, the effect of FT Processing Aides on the viscosity, spiral flow and selected mechanical properties (tensile properties and impact properties) are shown.

Materials

In the first experiments, a commercial 8 MFI polypropylene homopolymer from Sasol Polymers was used. The polymer was filled with 11% CaCO₃. An Engel injection molding machine was used. For the three experiments, the following additives and levels of addition were used:

- 1. Calcium stearate: 0.75%
- 2. Commercial FT Processing Aide: 0.75%
- 3. Commercial FT Processing Aide: 1.76%

The addition of FTPA aides could be a potential benefit in terms of lowering the energy required for processing and the benefits will be discussed in the next sections.

Results

Rheology measurements were performed on an Anton Paar MCR parallel plate Rheometer. Experiments were conducted at 190 °C and at 230 °C. It is expected that both calcium stearate and the FT Processing Aide will reduce the melt viscosity. The results are presented in Figure 1.

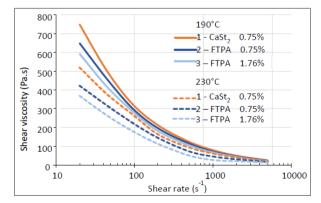
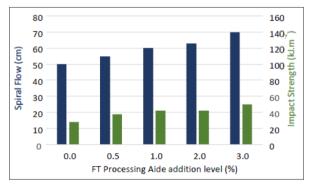


Figure 1: Viscosity Effects of 1) CaSt, 2) FTPA at 0.75% and 3) FTPA at 1.76% in PP at two temperatures

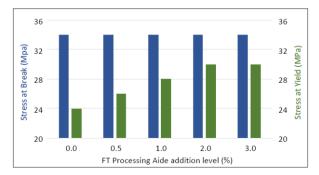
From Figure 1 it is evident that over the shear range studied, calcium stearate and FTPA lowered the shear viscosity with the FTPA outperforming CaSt at equivalent loadings. Increasing the level of FTPA resulted in a further lowering of the viscosity. It is evident that FTPA can decrease the viscosity of the polymer, which will ease the injection step, enable faster chain relaxation, allows faster flow into the mold form, and faster flow through runners.

FTPA consist of chains that are shorter than the average chain length of the polymer that is being injection molded. It is therefore important to ensure that the addition of FTPA does not result in a deterioration of the mechanical properties. Laboratory testing was carried out to quantify these effects and to investigate if the addition of these processing aides could improve certain properties. Marshall showed that the addition of these molecules (within a given range) did not result in a significant deterioration in the mechanical properties during injection molding [4]. Although not discussed further there, it was noted that FTPA addition would not result in a deterioration in optical, adhesion and printability properties [4]. The present work covers additional test to highlight the effect of the addition of these molecules on the process.

In Figure 2, the effect of the FTPA on spiral flow and impact strength is shown. Spiral flow is an indication of the ease of flow - the longer the spiral flow (in cm), the better the flowability. With increasing FTPA addition levels an increase in the spiral flow was obtained. This is in line with the viscosity measurements (Figure 1). It is evident that there was a marginal improvement in the impact strength.







In Figure 3, the stress at break and stress at yield results are shown.

Figure 3: Effect of the FT Processing Aide on Tensile Properties

The results in Figure 3 indicates that the stress at break results were consistent up to 3% FTPA addition. Interestingly, the stress at yield showed an increase. Up to 3% addition the FT addition had no negative influences on the tensile properties, with even a slight benefit in the stress at yield performance.

In Figure 4, the effect of FTPA on the spiral flow and impact strength of different PP homopolymers (MFI= 8 and 12) and a block copolymer (MFI=5) is shown.

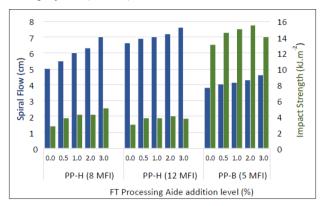


Figure 4: Effect of FT Processing Aide on two PP homopolymers (PP-H) and a block copolymer (PP-B)

The results in Figure 4 indicate that the FTPA provided benefits in various formulations ranging from unfilled PP to filled PP, and to both homopolymers and copolymers.

Optimization Needed When Adding FT Processing Aide

The addition of FTPA may not immediately result in a process improvement and needs to be done together with optimizing the injection molding process. The typical addition rate of FTPA to PP is 1-2%, but in some cases up to 4% can be added. As a first step, it is important to understand if the process is plasticization or cooling limited. Should the process be plasticization limited, the effect should be carefully observed before and after the introduction of the FTPA. It is important to check if there is a drop in the plasticization time before dropping the backpressure. This can be carried out in steps. The screw speed can also be increased, if required. If the cycle is governed by cooling time, FTPA can also assist in optimizing the process. After the addition of a FTPA, it may be possible to decrease the temperatures in the extruder and mold to obtain a lower melt temperature. FTPA addition will result in a significant reduction in the melt viscosity. In Figure 5, the effect of the addition of FTPA on the viscosity of a 2MFI resin is shown as a function of temperature. It is clear that the effect of the FTPA is seen across the temperature range.

It is important to note that the addition of FTPA needs to be carried out correctly and the machine parameters to be set correctly. The processing aide (which is in a solid, pastille form) can be blended with the polymer using conventional techniques, such as tumble blending, or via dosing directly into the extruder via micro-feeders.

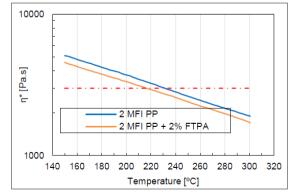


Figure 5: Effect of the Addition of FTPA on Melt Viscosity [4]

Summary of the Outcome of The Laboratory Investigations The main conclusions from the laboratory investigations and trials can be summarized as follows:

- FTPA acts as a viscosity modifier during the processing of polyolefins, allowing faster plasticization and quicker injection.
- The addition of FTPA allows for the use of lower temperature profiles and/or reduces cooling times. These factors ultimately result in faster cycle times during injection molding.
- Rates are typically increased by between 10% and 25% with no adverse effects on physical dimensions or mechanical properties of the molded articles.

Case Studies from the Field

In this section a number of cases of successful applications will be covered. It is evident that the FTPA could be used in both smaller and larger items to optimize the cycle times, to improve part quality, and address common in-process induced defects.

Case Study 1

In the first case study, the effect of the addition of FTPA on molding a car bumper was evaluated. The type and model number of the extruder was not disclosed. For this particular optimization the temperature profile was optimized by increasing the temperature in the first zone, while decreasing the temperatures in the other zones. The conditions and results are given in Table 2.

Table 2: Effect of FTPA	on the Number of Bumn	ers Produced
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	in on the ramber o	i bumpers Produced	
Parameter	Before FTPA Addition	Change after FTPA addition	
Temp. Profile (°C)	200-220-220- 210-200- 185	15-↓10-↓15-↓20- ↓15- ↓10	
Hot-runner (°C)	220-220-220- 220-220- 220-220- 220-220-2	-	
Cycle Time (s)	130.5	↓27.1 (21%)	
Cooling Time (s)	65	↓20 (26%)	
Back Pressure (%)	5-5-25	-	
Screw Speed (%)	75	-	
Melt Cushion (mm)	0.5	-	
Injection Pressure (%)	60-70-70-65-60	↑5	
Injection Time (s)	18	↓7 (39%)	
Hold-on Pressure (%)	35-35	-	
Holding time (s)	5	-	
Injection Speed (%)	70-75-80-70-55	-	
Plasticizing Time (s)	17.6	↓1.6 (9%)	
Silicone Spray	every 4 shots	-	
Part Ejection Temp. (°C)	50-70-46	marginal decrease	
Part Weight (g)	3400	↓15 (0.4%)	
Productivity (parts/hr)	27	↑8 (30%)	

By careful optimization, it was possible to produce 8 extra bumpers per hour, which is a productivity improvement of around 30%. Further, take note that the average part weight was reduced due to improved part tolerances which saves material.

Case Study 2

In the second example, the effect of FTPA on beer crate production is shown. For this example, the customer was interested in maximizing output while maintaining the quality of the crates. The temperature profile was optimized (Table 3). The results are presented in Table 4.

Table 3: Temperature Profiles with and without FT Processing Aide

Before FTPA addition

Defore F I FA addition							
Temp. profile (°C)	Set	204	240	249	248	199	
	Actual	204	239	249	248	193	
After FTPA addition							
Temp. profile (°C)	Set	180	198	230	205	190	
	Actual	183	207	228	210	189	

Table 4: Improvement in Cycle Time by Adding FTPA

PP used in the production of beer crates						
	Reference	2% FTPA				
Cycle time (s)	62 53					
Cooling time (s)	35 25					
Plasticization time (s)	27 24					
Parts per hour	58 67					
Productivity improvement	17%					

In this case, the addition of FT Processing Aide resulted in a 17% overall improvement in productivity.

Case Study 3

FT Processing Aide has been extensively trialed in garden and home furniture. Table 5 summarizes some examples, plus the benefits that were gained.

	Table 5: Summary of Other Examples of Efficiency						
	Description	FTPA addition rate	Cycle time reduction	Processing changes	Other benefits		
1	PP Garden Chair	+2%	11%	↓temp profile 20°C ↓back pressure 10% ↓cooling time 15%	Productivity †11%		
2	PP Garden chair	+3%	19%	↓back pressure 60% ↓plasticizing time 22%	Productivity †23%		
3	PP Garden chair	+4%	24%	↓temperature profile 10°C ↓back pressure 70% ↓plasticizing time 12% ↓cooling time 12%	Productivity †24%		
4	PP household chair	+3%	10%	↓temp profile 30°C	-Lower injection pressure -Reduce silicon spray 60% - Productivity↑10 %		
5	PP Household chair	+5%	9%	↓temp profile 20°C	-↓injection time 18% -↓hold time 18% -Eliminated silicon spray - Productivity↑9 %		
6	PP Medium chair	+5%	8%	↓temp profile 5°C ↓cooling time 15%	-Improved pigment dispersion -↓injection pressure -Eliminated silicon spray - Productivity↑8 %		

The results indicate that over a range of chairs, the FT molecules were able to provide significant cycle time reductions, allow for lower temperature profiles, and reduced pressures.

Cost in Use of FT Processing Aide in Injection Molding

A previous paper reviewed the financial benefits of the use of FT Processing Aide [4]. The injection molding industry is predominantly price sensitive, so any increase in production cost is closely scrutinized. Often costs are only considered to be input cost, be it raw materials or labor and utilities. It would, however, be better to consider unit cost to produce an article. A fair reflection would be to split the cost into 'machine cost' and 'material cost'. Although the additive may add cost to the 'material costs', the addition of FTPA could play a positive role in reducing the 'machine costs', be that by lowering electricity consumption or increasing output, thereby improving the productivity of the whole process. for "injection molded part cost" or "injection molded part cost reduction" yields numerous articles with strategies to reduce unit cost. Clearly, faster cycle time is promoted and partly achieved through good mold and part design as well as screw design and cooling. Material selection and use of a polymer processing aide has been proven to yield substantially faster cycle times and lower energy requirements. Processing aides which reduce cycle times yield reduction of the overhead and direct labor cost per molded unit. Meanwhile, even an increase in material cost due to use of a process aide yields lower cost per molded part. Faster processing with lower energy requirements can dramatically reduce production time, reduce number of machines, reduce direct labor cost, and help spread plant overhead costs. In the following examples, the use of Fischer-Tropsch as a polyolefin process aide shows lower cost to produce a variety of polyolefin articles.

In today's environment, overhead costs tend to exceed direct labor cost for injection molding operations. Internet searches

Polymer prices are as reported by Plastics News October 2020 [11]. HDPE Injection GP grade 76 cents/lb and PP Homo Injection GP grade 67 cents/lb. In Table 6, the potential cost saving per article for a few examples are shown.

Table 0. 1 offential Savings Obtained when using 1 1 1 offessing Alde							
	Polymer	Article weight in grams	Initial Cycle Time	Cycle time with FTPA	% lower Cycle Time	Savings per article	
Hinged closure	PP	12	11.8	10.2	-14%	5,34%	
Hinged Container	PP	80	17.9	15.9	-11%	6.88%	
Beverage Crate	HDPE	850	38	30	-21%	2.95%	
Dairy crate	HDPE	1800	51	48	-6%	2.49%	
12-bottle crate	HDPE	2100	57	50	-12%	2.86%	
Table	PP	3000	109	85	-22%	4.94%	
Fruit picking crate	HDPE	34000	156	130	-17%	3.82%	

Table 6: Potential Savings Obtained when using FT Processing Aide

Assumptions

Manufacturing cost assumptions; Direct Labor @ \$20/hour, Electricity @ \$0.08/kWh, faster production reduces operating days, plant base load for electricity unchanged.

In summary, FT Processing Aide can reduce direct processing costs, while also aiding in reducing overhead costs.

How can FT Processing Aides Aid in Sustainability?

The pressure on converters (and their customers) to be more sustainable is constantly increasing. Apart from recycling, there is also a drive to decrease the footprint from their processes. The ability to lower energy consumption and increase output rate could be used by converters to reduce their costs, and also have a positive effect on their environmental footprint. As shown in Table 5, this effect could be significant (productivity increases of more than 10% are typical). It is assumed that around 70% of the energy use of an injection molding machine is used for plasticization. The addition of FT molecules can, therefore, have a major influence on the energy consumption by allowing easier processing.

The reduction in scrap is also a potential environmental benefit that could be exploited. There is also the possibility to use a lower MFI polymer (with associated better mechanical properties), and then use the FT processing aide to improve the flow, thereby ensuring proper mold filling. These processing aides can also potentially be used to enable recycle content. Should the MFI of a recycle stream be too low, inconsistent, or containing polymer gels to be considered for injection molding, FTPA may aid the process.

Some additional benefits that were noted include:

- Improved mold release (compared to silicon sprays this results in a significant cost saving)
- FT Processing Aide can also be used to aid the dispersion of inorganic fillers, such as calcium carbonate, talc, etc., in polyolefins during compounding prior to injection molding.
- Easier de-molding may lead to faster cycle times
- Smoother surface finish and improved gloss
- Better pigment dispersion
- May enable reduction of the masterbatch concentration
- Reduced stress-whitening on ejection, leading to faster cycle times

Conclusions

Injection molding customers are under increased pressure to lower production cost and improve their environmental footprint. These two aspects can typically be achieved by using additive and/or investing in new equipment. This article summarizes several laboratory investigations and actual case studies on the use of FT molecules as internal processing aides.

Laboratory studies showed that FTPA can reduce the melt viscosity significantly, while (if added at concentrations below 4-5%) it will not significantly reduce the mechanical properties. Some mechanical properties may even show a slight improvement (e.g. stress at yield). The case studies showed that these FTPA can be used in many injection molding applications and result in a significant reduction in cycle time and energy consumed. It can also be a tool to improve the sustainability of the process by lowering the energy requirements and also by reducing the scrap rate and also the wear on the equipment, by reducing the friction and the back pressure in the injection molding equipment.

The addition of FTPA can, therefore, act as a versatile tool in optimizing the injection molding process.

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